University of Natural Resources
and Life Sciences, Vienna

Determination of Nickel release from ground basalt rock in agricultural soils and the accumulation of Nickel by crop plants

Master thesis

Submitted by

Katrin Ehrenbrandtner, BSc

Student ID: 01240320

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Supervised by:

Priv.-Doz. Dr. Markus Puschenreiter & Univ.Prof. Dipl.-Ing. Dr.nat.techn.Wenzel Walter

Institute of Soil Research,
Department of Forest- and Soil Sciences,
University of Natural Resources and Life Sciences, Vienna, Austria

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The earth is what we all have in common.

-Wendel Berry (goodreads, 2020)

Affidavit

I hereby declare that I am the sole author of this work. No assistance other than that which is permitted has been used. Ideas and quotes taken directly or indirectly from other sources are identified as such. This written work has not yet been submitted in any part.

Abstract

The aim of this work was to examine how much nickel and chromium is introduced into the soil by the addition of basalt stone meal from Pauliberg and a basalt stone meal + compost mixture with increased chromium and nickel values; furthermore it was assessed if the treatments influenced shoot concentrations of nickel, chromium and other elements in three different crop species. A pot experiment was carried out in which an equivalent of 5 t basalt meal (or 5.3 t/ha in the basalt meal-compost treatment) per hectare of soil was introduced into two different test soils. In addition, three different plants (wheat, spinach and soy) with different element mobilization mechanisms in the rhizosphere were planted. In some treatments, slight increases in the concentrations of nickel and chromium, but also of phosphorus were observed in the plants, with the latter being released mainly from the compost fraction. Only minor and negligible changes were observed in the mobile fractions of chromium and nickel in the soil extract. The addition of basalt stone meal as a soil additive or in composting is harmless with regard to the possible release of nickel or chromium. Nevertheless, due to its high nickel and chromium concentrations, basalt stone meal from Pauliberg is not permitted as a soil- or plant additive according to the Austrian fertilizer ordinance. A possible and legal application of the basalt stone meal is as an additive to compost. This work should be followed up by a longer field trial where higher application rates and the effects on soil and plants should be tested.

Kurzfassung

Diese Arbeit hat das Ziel zu überprüfen wie viel Nickel und Chrom durch die Zugabe von Basaltmehl vom Steinbruch „Pauliberg" und einer Basaltmehl-Kompost-Mischung mit erhöhten Chrom- und Nickelwerten in den Boden eingetragen werden und wie viel davon von verschiedenen Nutzpflanzen in ihre oberflächliche Biomasse aufgenommen wird. Dazu wurde ein Topf-Experiment durchgeführt, wo ein Äquivalent von 5 t Basaltmehl (bez. 5,3 t/ha in der Basaltmehl-Kompost Variante) pro Hektar Boden in zwei unterschiedliche Versuchsböden eingebracht wurde. Des Weiteren wurden drei verschiedene Pflanzen (Weizen, Spinat und Soja) mit unterschiedlichen Element-Mobilisierungsverhalten in der Rhizosphäre gepflanzt, um zu überprüfen, ob es Unterschiede in der Mobilisierung und der Aufnahme von Nickel und Chrom in die Biomasse gibt. In einigen Behandlungen wurden in den Pflanzen geringfügige Anstiege der Konzentrationen von Nickel und Chrom, aber auch von Phosphor beobachtet, wobei letzteres vor allem aus dem Kompost-Anteil freigesetzt wurde. Bei den mobilen Anteilen von Chrom und Nickel konnten im Boden-Extrakt nur geringfügige und vernachlässigbare Veränderungen festgestellt werden. Die Zugabe von Basaltmehl als Bodenhilfsstoff oder in der Kompostierung ist im Hinblick auf die mögliche

Freisetzung von Nickel oder Chrom unbedenklich. Dennoch ist das Basaltmehl vom Pauliberg durch seine hohe Nickel- und Chromkonzentrationen gemäß österreichischer Düngemittelverordnung nicht als Boden- oder Pflanzenhilfsstoff zulässig. Eine mögliche Anwendung des Basaltmehls wäre jedoch als Zuschlagsstoff zu Kompost. Es sollte auf diese Arbeit noch ein längerer Feldversuch folgen, wo auch höhere Ausbringungsmengen und deren Auswirkungen auf Boden und Pflanzen überprüft werden.

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List of Abbreviation

B	Basalt stone meal
BC	Basalt stone meal+ Compost
DM	Dry Mass
M	Moosbierbaum (Soil)
G	Gföhl (Soil)
LOQ	Limit of Quantification
LOD	Limit of Detection
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
NT	No treatment
NP	No plant
So	Soy
Sp	Spinach
W	Wheat

1. Introduction

Erosion, acidification, and biological degradation are the top threats to the arable soils of our planet. Intensive agricultural practices are removing nutrients without adequate replacement, resulting in a continuous degradation of fertile soil (Cakmak, 2002). Except for nitrogen, all 18 elements essential for higher plants, originate from naturally occurring rocks and minerals. However, these nutrients contained in primary and secondary minerals are not easily available for plant uptake. The nutrients must be released through weathering. The continuous weathering of finely ground rock material (stone meal), applied on arable land, could remineralize the soil with a wide range of micro and macro nutrients, whilst most of the commercially available fertilizers mainly supply the soil only with the main macronutrients N, P and K and depletes the soil of other nutrients and trace elements over a long period of time (van Straaten, 2006). The application of stone meal on arable land has the goal to restore nutrients in leached and degraded soils over a longer period, through imitating natural geological processes (Leonardos et al., 2000).

Basalt is characterized by a high weathering rate and is widely recognized as producing productive soils. Basalt stone meal contains at least 6 plant-essential nutrients, including P, K, Ca, Mg and Fe (Beerling et al., 2018). The basalt stone meal used in this experiment has an above average Ni and Cr concentration and by applying it to the field there is a risk of accumulation in the soil and the plants growing on this fields. This process is depending on the weathering rate. In tropical regions the weathering rate is much higher and the nutrients but also the heavy metals are faster released than in temperate climates (de Villiers, 1961). Nickel is an essential micronutrient for many higher plants and some animal species. There is no data proving that it is essential for humans. As for most metals, the toxicity of Ni is dependent on the route and amount of exposure and the solubility of the Ni compound (IARC, 2012). There is no maximum level for Ni (European Food and Safety Authority, 2015) or Cr (European Food and Safety Authority, 2014) in food.

Latest findings show that basalt stone meal can also be used for CO_2 sequestration. A study from Kelland et al. (2020) showed a new and promising use of basalt stone meal. They added 10 kg/m^2 basalt stone meal to arable soil and not only did the crop biomass increase but also the carbon capture potential was four times higher than in the soil without basalt stone meal added.

Stone meals in agriculture are mostly used in organic agriculture (Snoek and Wülfrath, 1995). The organic farming area in the EU covers an area of about 13.4 million hectares of agricultural land (Eurostat,2020b) and has risen by 7.5% since 2012, in Austria even by 24% since 2012 (Eurostat, 2020a).

1.1 Stone Meal

Crushed rock with a particle size under 0.2 mm is referred to as stone meal. Stone meals are made of almost every rock type like phosphate, carbonate, or silicon rock. Often bentonite and zeolite or volcanic ash are also used as stone meal (Fragsteiner, 1982). Stone meals have different functions. One of the main uses is to improve the soil conditions. It can be used to supply soils with minerals and to improve sandy soils or heavy chernozems by adding very fine particles with the stone meals. Stone meals high in silicate increase the buffering capacity. In combination with added humus the formation of clay-humus-complexes is triggered (Snoek and Wülfrath, 1995). By adding high amounts (50-900 t/ha) of stone meal in the course of a few years, soil texture can be improved, and the aeration and workability of the field are increased (Snoek and Wülfrath, 1995). By adding several tons of stone meal per ha, the water holding capacity, the pH value and the sorptive capacity could be increased. Furthermore, the nutrient leaching was reduced and thus an increase in yield on sandy soils was achieved (Pfeiderer, 1986).

In agriculture stone meals are used, mostly in organic agriculture, in fruit production and home gardening. In conventional agriculture it is not often used because of the high transport and storage costs (Snoek and Wülfrath, 1995).

In addition, stone meals can also be used as additives to organic materials. Snoek and Wülfrath (1995) mentioned that stone meal can be added to different types of compost where it helps to develop a high-quality fertilizer, and to slurry and solid manure where it helps to bind ammoniac and promotes a faster decomposition.

The application of stone meals should help to stabilize the nutrient- and water availability in the soil. Trace elements and clay minerals are added to the soil which could be beneficial for humans and animals consuming the enriched plants (Henning, 1981).

Stone meals can be classified into different particle size categories. The finest category of stone meals has an average particle size 2 to 3 µm. The categories go up until the average particle size reaches 0.2 mm (Snoek and Wülfrath,1995). The effects of the stone meal are timely correlated with the particle size of the stone meal - the smaller the particle the larger the surface area and the faster the mobilization of the nutrients and trace elements in the soil begins (Snoek and Wülfrath,1995). However, according to Blum et al. (1989b), the development of nutritional value depends above all other factors on the mineral composition and the degree of grinding and not as much on the nutritional element total content.

1.2 Legal Regulations Austria

In Austria stone meals are declared as soil additives and are under the fertilizer regulations of Austria. As soil additive defined are all materials without notable nutrient content, that do not harm humans, animals, or the ecosystem (Düngemittelverordnung, 2004).

In Austria there are three types of regulations which concern the use of stone meal as an additive in agricultural practice.

First, fertilizers have limit values on their heavy metal concentrations and second, if a soil additive is approved to be sold, there are limits of heavy metal concentrations that are allowed to be spread per ha, which must not be exceeded by maximum application quantity.

The limit value of nickel and chromium are 100 mg nickel and 100 mg chromium per kg fertilizer DM for the use on agricultural land, whereas the maximum application quantity of heavy metals immitted by fertilizers and soil additives are not allowed to exceed 200 g nickel per ha and year and 300 g chromium per ha and year, at maximum application quantity. The maximum application quantity must be labelled on the product (Düngemittelverordnung, 2004). Summarized there is a regulation on the concentration of a heavy metal in the product and how much of a heavy metal is allowed to be immitted into the soil using that product.

Third, there also are regulations on heavy metal concentrations in different compost additives, which are noted in the “Kompostverordnung” of Austria. For the use of basalt stone meal as an additive to compost, there is no special requirement on quality or limits on heavy metal concentrations, other than that the limit values on various heavy metals do not exceed the concentrations stated in the regulation. The nickel and chromium concentrations in the final product must not exceed 100 mg/kg DM nickel and 250 mg/kg DM chromium (Kompostverordnung, 2001).

1.3 Research questions and objectives

In Austria stone meals are declared as soil additives and not as fertilizers. Fertilizers have limit values on their heavy metal concentrations. Soil additives fall into this category. The limit value of nickel and chromium are 100 mg nickel and 100 mg chromium per kg fertilizer DM for the use on agricultural land. (Düngemittelverordung, 2004).

A recent assessment (Scheidl, 2015) showed that the stone meal from Pauliberg had a nickel concentration of 334 mg/kg DM which was more than three times higher than the limit value approved for fertilizers. Also, the chromium concentration was with 191 mg/kg DM almost twice as high as the allowed value.

This thesis firstly aims to ascertain if the high nickel and chromium concentrations in the basalt stone meal form Pauliberg are a risk for accumulating heavy metals in the soil and the crops growing in the soils where the basalt stone meal is used. Secondly, if there is a difference between different crops because higher plants can considerably effect the dissolution of basalt rock and need to be taken into consideration when assessing the cycle for micro- and macro nutrients (Hinsinger et al., 2001).

Research questions:

Q1: How much Ni and Cr are released into the soil, using an agricultural conventional amount of Pauliberg stone meal?

Q2: Is there a significant difference in Ni and Cr release and plant uptake cultivating different crops?

Q3: Does the addition of compost influence the Ni and Cr release into the soil and the uptake of the plants?

Hypotheses:

H1: The addition of Pauliberg stone meal increases the Ni and Cr content in the soil and crops.

H2: Pauliberg stone meal mixed with compost increases the Ni and Cr content in soil and crops in comparison to stone meal only treatment.

H3: The addition of Pauliberg stone meals does not increase the bioavailable fraction of nutrients and trace elements in the soil, also not by adding compost to the soil.

2. Materials and Methods

To answer the research questions a pot experiment was set up. In chapter 3.1 to 3.4 the components that were chosen for the experiment are described in detail. In chapter 3.5 the setup of the experiment and the harvesting method are discussed. The last two chapters of Materials and Methods present the extraction methods and the methods of the chemical analysis used.

2.1 Basalt Stone Meal

The basalt stone meal used in this experiment stems from the quarry “Basaltwerk Pauliberg” in Landsee, Burgenland, Austria. The area is characterized by volcanic activity in the young tertiary and “Pauliberg” itself is a remnant of a volcano that was active 11 million years ago (Weixelberger, 2017).

Table 1 shows the main components of the basalt found at this site and its heavy metal contents. The nickel concentration of the stone meal is 334 mg/kg dry mass, which is three times higher than the national fertilizer regulation were the nickel concentration is limited to 100 mg/kg fertilizer (Düngemittelverordnung, 2004).

Table 1 Main Components Basalt meal (Scheidl, 2015)

Main components %		Selected heavy metals mg/kg DM	
Silicon	20.6 - 21.8	Barium	83
Iron	8.3 - 9.1	Lead	< 0.1
Calcium	7.3 - 7.5	Cadmium	< 0.1
Aluminum	6.5 - 7.1	**Nickel**	**334**
Magnesium	4.3 - 5.0	**Chromium**	**191**
Sodium	2.6 - 2.2		
Titanium	2.1 - 2.2		
Potassium	0.7 - 1.5		

66% of the particles of the stone meal are sand and 2.4% of the particles are clay (Sayedahmed,1993). Using the finger test Snoek and Wülfrath (1995) described most of the particles of the stone meal are less than 0.05 mm.

2.2 Compost

The compost used in the experiment was provided by the Esterhazy Betriebe GmbH from Burgenland. The composition of the compost is shown in table 2. The extraction method used was a plant digest in concentrated HNO_3. The element concentrations in digested compost were measured on ICP-MS and ICP-OES.

Table 2 Compost Composition measured on ICP-MS and ICP-OES. Extraction Method: Plant digest in concentrated HNO_3

Macro Elements g/kg		Micro Elements mg/kg	
P	9.54	Co	6.45
Mg	15.23	Ni	21.02
K	17.96	Cu	22.97
F e	18.07	Zn	103.64
Ca	64.29	As	8.16
Al	14.25	Mo	10.55
		Cd	0.24
		Pb	12.37

2.3 Soils

Two soils were chosen that represent two very common Austrian agricultural soil types regarding their composition and acidity. There are indications that distinct rhizosphere processes such as pH changes the heavy metal mobility in the soil and thus plant uptake (Qi Tang Wu et al.,1989)

Soil G is an acidic sandy soil from Gföhl (Waldviertel), developed on crystalline rocks (Waldviertel, Mühlviertel, Bucklige Welt, etc.). The pH ($CaCl_2$) is 5.5, the texture is sandy with a maximum water holding capacity of 35%.

Soil M is a carbonate silt-clay soil from Moosbierbaum (Tullnerfeld), representing Austrian soils that developed on limestone (Alpenvorland, Marchfeld, Wiener Becken). The pH ($CaCl_2$) is 7.32 and the texture is clayey with a maximum water holding capacity of 65%.

2.4 Plants

This chapter defines why wheat, soy and spinach had been chosen for this pot experiment. They each have different rhizosphere processes that effect the Ni and Cr mobilization differently and are described in the following three paragraphs. Root exudates might affect heavy metal mobility in the soil and the plant uptake (Mench and Martin, 1991). Figure 1 shows the three different plants.

2.4.1 Wheat

Wheat as a member of the Poaceae family releases Phytosiderophores (PS) for the acquisition of iron (Fe). Phytosiderophores are root exudates (Marschner et al, 1986), and have a high affinity for Fe and other metals and can thus solubilizes elements like Cu, Zn and Ni (Murakami et al., 1989). This might lead to higher Ni uptake in the plant biomass than other crops. For this experiment winter wheat was used of the variety “Winterweizen gr70”.

2.4.2 Soy

Legumes often accumulate most of their N through symbiotic N_2 fixation. This leads to excess uptake of cations over anions and therefore to a net efflux of H_3O^+ ions in the rhizosphere and the pH is decreased in the rhizosphere (Haynes, 1983). Nyastanga and Pierre (1973) showed that the growth of soy for 72 days under glass house conditions was sufficient to lower the pH by more than one unit. The acidification could lead to higher mobilization of heavy metals in the rhizosphere.


Figure 1 Pictures of the Pot Experiment (wheat, soy, spinach)

2.4.3 Spinach

Kloke et al. (1984) classify spinach as “high” in the relative accumulation of heavy metals in the plant parts of different crops. Lübben (1993) showed the highest transfer rate of Ni, Cd, Zn, Cu, Pb and Cr are from the soil to the leaves of spinach and lettuce and the roots of various plants. Compared to fruit and crops, heavy metals easily accumulate in leafy part of vegetables (Mapanda et al., 2005). Since with spinach only the leaves are eaten the heavy metals easily transfer into the human diet. The spinach used was from the variety “Matador Sp10”.

2.5 Pot Experiment

A pot experiment was conducted with the soils and plants described in the chapters above. The pot experiment was set up in the greenhouse of the UFT building in Tulln and the light intensity, humidity and temperature were kept the same throughout the experiment. The two soils “Moosbierbaum (M) “ and “Gföhl (G)” were tested with added basalt stone meal (B) (0.895g/pot), with a combination of basalt stone meal (0.945g/pot) and compost

(6.75g/pot) (BC) and without anything added (NT-Control). The amount of stone meal used was calculated considering conventional used amounts of stone meal used on fields. The amount varies between 2 and 10 t/ha/year (Blum et al.,1989a). For this experiment a distribution of 5 t/ha/year was assumed. This led to the following calculation: soil density: 1.4 kg/dm^3; intermixing depth: 2 dm; distribution: 0.5 kg/m^2

$10 \times 10 \times 2 \times 1.4 = 280\ kg$ soil/m^2

$0.5\ kg \div 280\ kg = 0.00179\ kg\ = 1.79\ g$ stone meal/kg soil

The amount mixed in with the compost was calculated by a 1:10 volumetric ratio of basalt stone meal and compost (Sonnenerde,2020), which led to an addition of 13.5 g compost + 1.89 g rock flour per kg soil.

Each pot contained 500g of soil and all treatments were set up in four replications. Each configuration was mixed in 4 kg batches for each pot to contain the same mixture. In table 4 all the configurations are listed.

Table 3 Abbreviations Configurations pot experiment

M	Moosbierbaum
G	Gföhl
W	wheat
So	soy
Sp	spinach
NT	No treatment
B	basalt stone meal
BC	basalt+compost
Np	No plant

Figure 2 Greenhouse Pot Experiment UFT Tulln

Table 4 Configurations pot experiment and overview on treatment abbreviations.

Plant / Soil	Wheat	Soy	Spinach	No Plant
Moosbierbaum	MWB MWBC MWNT	MSoB MSoBC MSoNT	MSpB MSpBC MSpNT	MNpB MNpBC MNpNT
Gföhl	GWB GWBC GWNT	GSoB GSoBC GSoNT	GSpB GSpBC GSpNT	GNpB GNpBC GNpNT

Each plant was tested in combination with all soil treatments; furthermore, unplanted pots were included as controls for assessing plant-specific effects on the soil. There were 48 pots per soil type and 36 of these contained plants. The plant seeds were geminated in petri dishes and on the 20.11.2019 were transferred to the pots. There they grew at 22°C at day and 20°C at night until the 22.01.2020. The lighting exposure was 14 hours a day. The soil moisture was kept at 80% water holding capacity. At the harvest (22.01.2020) the SPAD-value of the plants in each pot was measured by measuring the value of five leaves of each plant and calculating the mean value. The next step was to photograph the plants and count the number of shoots per pot. After that, the plants were cut 0.5 cm above the soil and washed with deionised water. Then they were dried in the oven at 80°C in paper bags for 24 hours. The dried biomass was first weighed and then milled in a plant mill. The plant biomass was calculated by the mean values of the number of shoots per pot and in the next step the mean value of the four replications. The plants were stored in paper bags for further analysis. The first 1-2 mm of the soil in the pots were removed and the rest of the soil samples were air-dried and sieved <2mm.

2.6 Extraction Methods

Every extraction procedure was quality controlled with 10% blanks and reference-soils and -plants each. For the blanks and references the same background solutions were used. The filters used to filter all the extracts were Munktell filter papers (grade 14/N). The aqua regia soil digest was used to determine how the different treatments of the soil effect the element concentrations in the soil. The 1 M ammonium-nitrate-extraction was performed to measure the differences in easily extractable metals influenced by different soils, treatments, and plants. To determine the different element concentrations in the three different agricultural plants a plant digest in concentrated HNO_3 was conducted.

2.6.1 Aqua Regia Soil Digest ÖNORM L1085

The Aqua regia soil digest was performed on the Microwave type „MARS 6 System “, CEM GmbH. It was performed with the program “aqua regia” with a ramp time of 45 min and a cool down time of 15 min. The samples were left open overnight under the fume hood after adding the soil samples and the acids into the microwave vessels. The next day the vessels were closed and put into the microwave. After the end of the “aqua regia” program water was added to the samples and after shaking and filtering they were filled into sample vials for further use. The microwave vessels are the Xpress Vessels and rotary for the microwave, CEM GmbH. The ramp time was 10 min and the hold time was 20 min at 1.200 W and a temperature of 200° C.

2.6.2 1 M Ammonium Nitrate Extract DIN 19730

This Method is used to determine labile metal fraction in the soil. Therefore, the soil was sieved <2 mm and 10 g of soil on a dry weight basis is added to an acid washed shaking bottle. Then 25 ml of 1 M NH_4NO_3 – solution was added to the bottles and the samples were shaken for two hours in an end-over-end shaker at 20 revolution per minute. After shaking the samples settled for about 15 minutes and were then filtered and acidified with 0.5 ml superpure HNO_3 to stabilize the samples for storage at room temperature until further use.

2.6.3 Plant digest in concentrated HNO_3

For the plant digestion in the microwave the protocol “Microwave digestion” of the Department of Crop Science, University of Natural Resources and Life Sciences, Vienna, was followed. 150 mg +/- 10 mg finely ground, and oven dried plant sample was weight into an Xpress Vessel (CEM GmbH). The samples were spiked with 3 ml superpure 65% HNO_3 and left under the fume cupboard overnight. The next morning 0.76 ml of H_2O_2 (30%) were added to each vessel and the vessels sealed and put into the microwave. The microwave used was the “MARS 6 System “, CEM GmbH spectrophotometer with room for 40 vessels. To digest all plant samples three rounds of microwave digestion were necessary, each with three blanks and three reference plant samples to go along with the plant samples. The program “plant material 2” was used as described in the protocol of the Institute of Agronomy of the University of Natural Resources and Life Science, Vienna. The ramp time is about 20 to 25 min and the hold time is 20 min at a temperature of 200°C and 1080 W. The process took about 1.5 hours and after that the vessels were taken out of the microwave and put back in the fume cupboard and 40 ml of HQ water were added to each sample. The samples then were shaken, filtered, and filled into sample vials.

2.7 Chemical Analysis

The elemental analysis was performed either on the ICP-MS (plant digest, aqua regia, ammonium nitrate extract) or the ICP-OES (plant digest, aqua regia). The measurements were performed by a task force member of the Institute of Soil Research, University of Natural Resources and Life Science, Vienna.

2.7.1 ICP-MS

ICP-MS stands for inductively coupled plasma-mass spectrometry. The ICP-MS (Elan 9000 DRCe, Perkin Elmer) used $_{115}$In as internal standard for the chemical analysis. Quality control and blanks were measured every 10th sample and at the end of each batch. Also reference soils and plants were measured. Obtained values were blank corrected.

2.7.1 ICP-OES

ICP-OES stands for inductively coupled plasma-optical emission spectrometry. The instrument used was a Perkin Elmer Optima 8300 ICP-OES. Internal standard with yttrium were used. Quality control and blanks were measured every 10th sample and at the end of each batch. Also reference soils and plants were measured. Obtained values were blank corrected.

2.8 Statistical Analysis

The soil results presented from the aqua regia soil digestion are the mean values of two replicates ± standard deviation. The other soil and plant results presented are the mean values of four replicates ± standard deviation. For the statistical analysis, the open source software “R-Commander” was used. To identify significant differences between the two different treatments and the control group a one-way analysis of variances (ANOVA) was performed on each soil and plant variable. To graphically illustrate the results “SigmaPlot 12.5” (Systat Sofftware Inc.) was used.

3. Results and Discussion

This chapter includes the results of the analyses and the interpretation of these results. The focus of the interpretation lies on the heavy metals nickel and chromium and the possibility of the accumulation of those elements in the soil or plant biomass and the risk of exceeding the Austrian limit values.

3.1 Total concentration of selected elements of the test soils in aqua regia extract

Table 5 Total concentration of selected macro-elements of the experimental soils (M, G) soils (in aqua regia extract. Showed are the 2 treatments ((B and BC) and the control (NT). Values are reported in means (n=2)

	K	Mg	Na	P	Fe	Ca	Al
				g/kg			
M	3.98	9.845	0.51	0.79	17.5	24.79	16.5
M-B	4.13	11.09	0.53	0.79	15.61	23.96	14.54
M-BC	4.2	10.08	0.55	0.85	17.58	25.29	16.60
G	3.95	5.22	0.50	0.58	22.20	3.01	16.70
G-B	3.96	5.25	0.50	0.58	21.79	2.1	16.13
G-BC	4.54	5.95	0.54	0.68	22.46	3.24	13.88

The two treatments (B and BC) did not have any effect on the total macro element concentration of the two test soils (M and G) (table 5). It is worth mentioning that for Fe, Ca, and Al, in the M-B and G-B, lower elemental concentrations were measured than in the soils without any treatment. Not one of these differences was statistically significant, therefore these findings could be just random or a dilution effect. Sayedahmed (1993) found, that the concentrations of Ca, K, Mg and Mn changed significantly after year two and three of the experiment of adding 5 or 10 t of basalt stone meal per ha soil.

Table 6 Total concentration of selected micro-elements of the experimental soils (M, G) in aqua regia extract. Showed are the 2 treatments (B and BC) and the control (NT). Values are reported in means (n=2). Background values are from Schwarz und Freudenschuss (2004) for arable land. The limit values are taken from the OENORM (2000) for arable land and home gardening.

	As	Cd	Cr	Cu	Ni	Pb	Zn
				mg/kg			
M	9.011	0.190	38.98	15.169	22.873	13.497	54.807
M-B	9.072	0.183	41.62	15.150	23.176	14.325	55.322
M-BC	9.151	0.180	39.71	14.866	22.998	13.540	55.178
Background values (pH > 7)	14.7	0.3	55	32	37	26	102
G	2.848	0.21	42.976	16.892	21.671	12.408	69.906
G-B	2.838	0.21	43.813	19.195	22.071	12.514	68.325
G-BC	2.220	0.21	38.505	20.032	21.963	13.251	71.290
Background values (pH > 5-6)	14.0	0.4	54	34	34	25	95
Limit values	20	0.5	100	100	100	100	150

Table 6 shows that the addition of stone meal (B) and the stone meal-compost–mixture (BC), did not have any significant effect on the total concentrations of micro-elements. The Cr and Ni concentration decreased in the BC treatment in comparison to the B only treatment, both in the M and G soil. The micro-elemental concentrations were all in the range of typical background concentrations of Austrian soils and well below the limit values for Austrian agricultural soils.

To reach the limit value for agricultural soils for nickel by adding 5 tons of Basalt stone meal per hectare and year, it would take 129 years for the M soil and 131 years for the G soil. For the BC treatment it would be exactly as long as for the B treatment. For the chromium it would take even longer, 171 years for the M soil and 164 years for the G soil to reach the limit value on chromium in agricultural land. The calculations can be found in the annex.

0.6 mg nickel per kg soil were added in the B treatments but the aqua regia digest only measured an addition of 0.3 mg/kg in the M soil and 0.4 mg/kg in the G soil. The slight deviation from the calculated increased Ni concentration derives from analytical uncertainties.

At a pH of 5.5 Cr_{3+} is almost completely precipitated. It needs very acidic soils to be slightly mobile. Only the Cr_{6+} is mobile (Broadly et al., 2012). The two test soils M and G have pH ($CaCl_2$) values higher than 5.5, therefore the chromium should not be very mobile.

The elements Mo, Cd and Pb were also measured in the aqua regia extract but the concentrations were below the LOQ and the Mn concentration was over the highest standard.

The compost regulation in Austria states that a maximum of five mass percent of additives (stone meal) can be added to the compost. There are no regulations on the heavy mental concentrations of the basalt stone meal as long as the end products nickel concentrations are below 100 mg/kg DM and the chromium concentrations are less than 250 mg/kg DM. In this experiment 1.89 g of basalt stone meal were added to 13.5 of compost, which are 14 mass percent and 46.76 mg of Ni per kg compost DM (334 mg/kg Ni DM *0.14). So, 140 g of stone meal and the 860 g of compost with 18.08 mg Ni per kg DM (22.02*0.86) add up to 64.84 mg Ni per kg DM of the compost product. The Ni concentration was under the limit value of the compost regulation. If the 5 mass percent of basalt stone meal were added to the compost used in this experiment, the Ni concentration in the product would be, with 37.72 mg Ni per kg DM (16.7 mg Ni in 50 g stone meal added to one kg DM compost with 21.02 mg/kg Ni), way under the limit value of 100 mg/kg DM in compost. The basalt stone meal form Pauliberg could be used as an additive to compost and the limit concentrations of Ni and Cr stated in the compost regulations of Austria would not be exceeded by adding 5 mass percent of the basalt stone meal used in this experiment, given that the compost raw material does not have very high heavy metal concentrations on its own.

3.2 Shoot biomass and SPAD-Value

Figure (3 – 5) show the above ground shoot biomass of soy, spinach and wheat planted in the two experimental soils. The two treatment B and BC did not have a significant effect on the shoot biomass. The biomass on the G soil was higher in all the plants, even though, as seen in table 5 above, the nutrient composition in both soils were similar. The higher biomass might be due to the different textures of the soils. Over time, watering the M soil led to the formation of a silt - and clay-rich layer on the soil surface, which has apparently limited the plant growth.

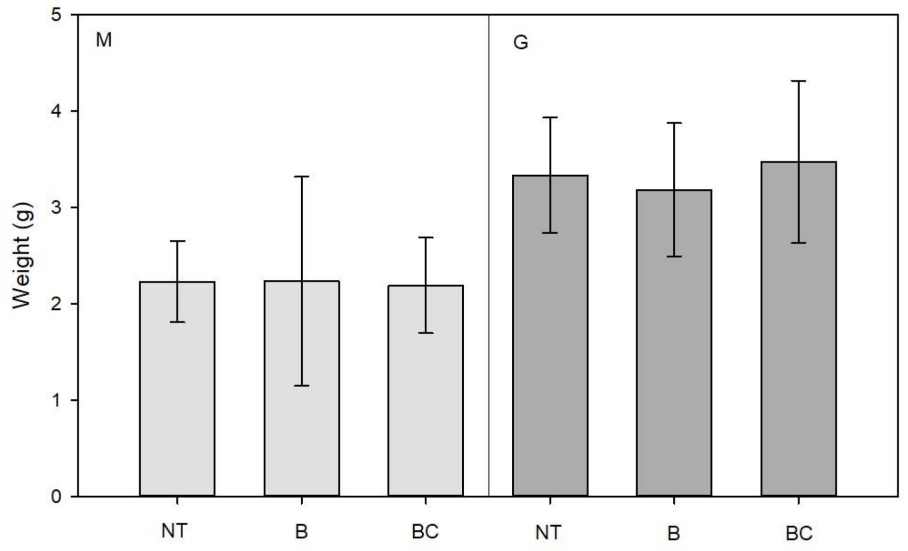

Figure 3 **Soy** shoot biomass (DM) in M and G soil with the treatments : Basalt stone meal (B), Basalt stone meal+Compost (BC) and no treatment (NT), Error bars indicate the standard error of the mean (n=4).

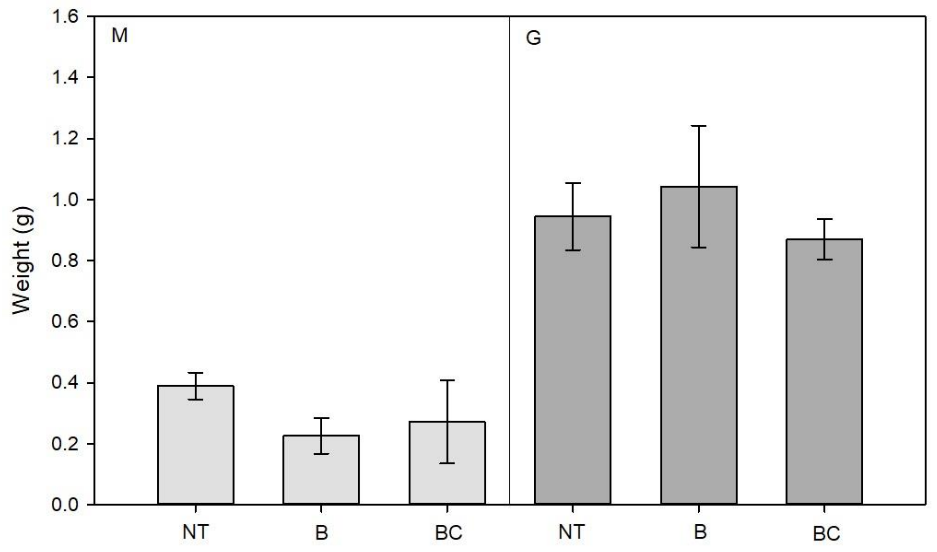

Figure 4 **Spinach** shoot biomass (DM) in M and G soil with the treatments : Basalt stone meal (B), Basalt stone meal+Compost (BC) and no treatment (NT), Error bars indicate the standard error of the mean (n=4).

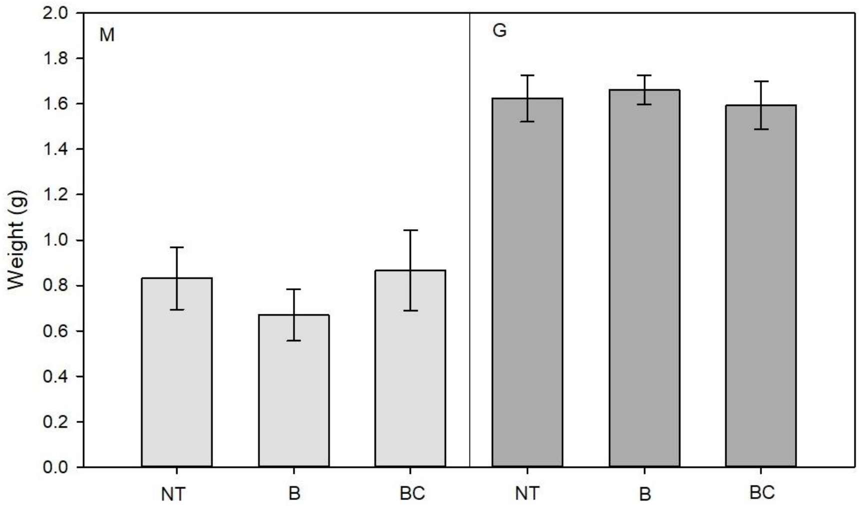

Figure 5 **Wheat** shoot biomass (DM) in M and G soil with the treatments : Basalt stone meal (B), Basalt stone meal+Compost (BC) and no treatment (NT), Error bars indicate the standard error of the mean (n=4).

The shoot biomass of spinach on the M soil tends to be lower in the B, and BC treatment than in the control (NT). This might be due to the adsorption of micronutrients on the stone meal and therefore decreased bioavailability, but it cannot be derived from the data.

It is noticeable that the BC treatment with compost added did not have any significant effect on the shoot biomass. This could be because the two soils used are from sufficiently fertilised fields and therefor by adding only a small amount of nutrients to the self-saturated soils, the effects of the compost are negligible. Rasp (1974) could not find any yield differences by adding stone meal to compost. The soil analysis showed that the nutrient concentrations of the compost were so high that the addition of stone meal could not change them.

Sayedahmed (1993), tested the basalt stone meal from Pauliberg on its effect to increase yields in different crops. There was no significant increase in shoot biomass. Also, Blum et al.(1989a) tested the basalt stone meal from Pauliberg on its use as a fertilizer and concluded that with this nutrient composition and used with the same amount as a mineral fertilizer the effects were extremely low. This is consistent with our biomass results.

The SPAD-Values of the different plants did not show any significant differences between the treatments (B, BC, and NT) and are shown in the annex.

3.3 Concentrations of Nickel, Chromium, and other trace elements in shoot biomass

The Ni concentration in the plant shoot biomass ranged from 2.3 mg/kg in wheat to 8.2 mg/kg DM in spinach (figure 6-8). The Ni concentrations were not significantly different for the two treatments (B and BC) and the control (NT). This means that neither of the two treatments had an effect on the Ni concentration in the shoot biomass of soy, spinach, and wheat.

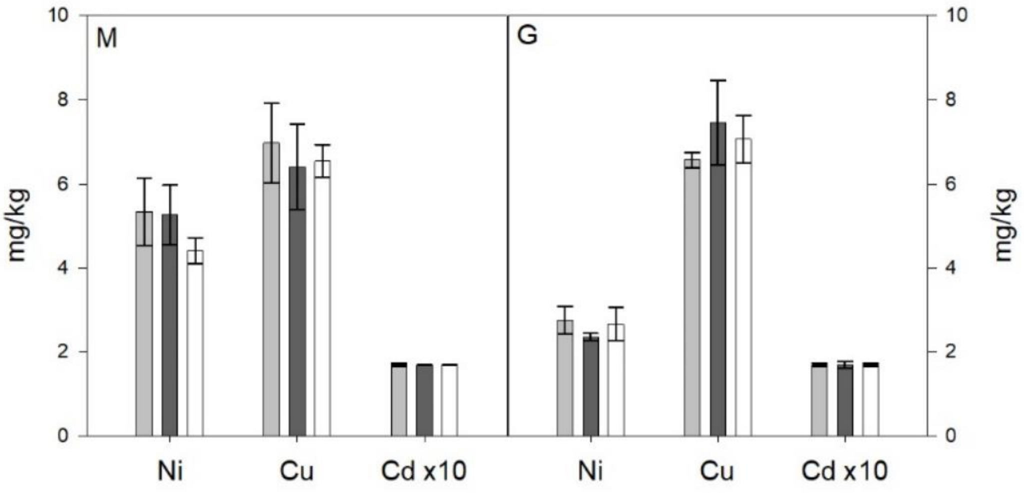

Figure 6 Concentration (in mg/kg) of nickel (Ni), copper (Cu), and cadmium (Cd) **in shoot biomass of soy** planted, in M and G soil. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The cadmium concentrations were multiplied by 10 for better readability.

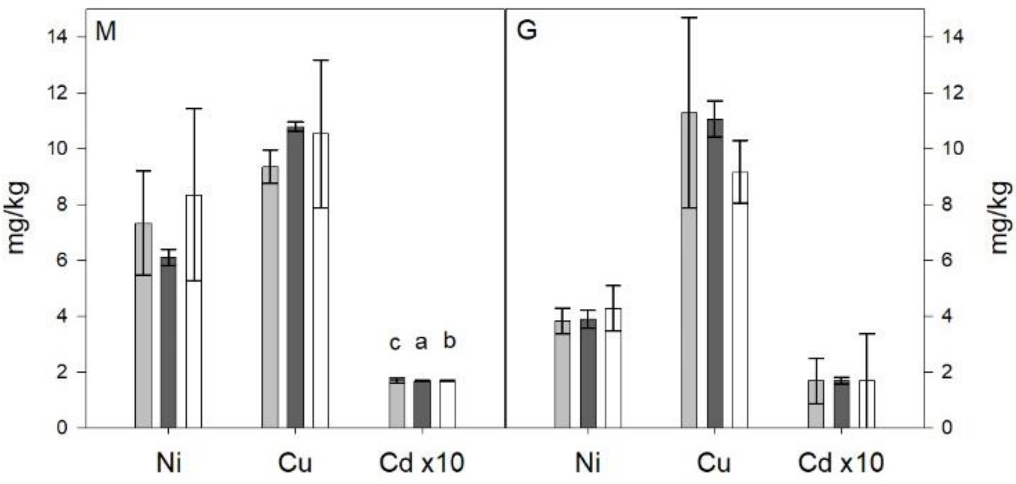

Figure 7 Concentration (in mg/kg) of nickel (Ni), copper (Cu), and cadmium (Cd) **in shoot biomass of spinach, planted in M and G soil**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The cadmium concentrations were multiplied by 10 for better readability.

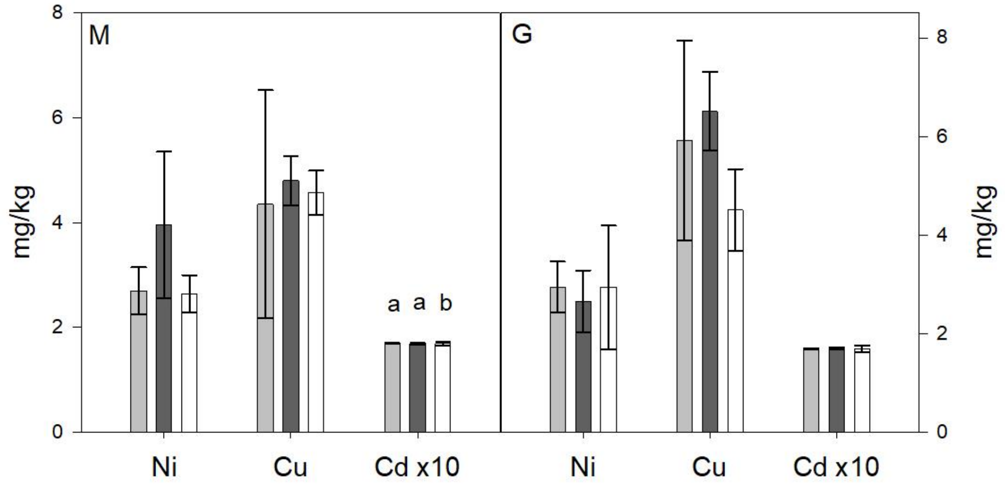

Figure 8 Concentration (in mg/kg) of nickel (Ni), copper (Cu), and cadmium (Cd) **in shoot biomass of wheat planted, in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The cadmium concentrations were multiplied by 10 for better readability.

Some treatments (wheat on M soil with BC-treatment; soy on M soil with B-and BC-treatment) showed a tendency of slightly increased Ni-values. Despite the lower biomass of the plants grown on M soil, the Ni concentrations in spinach and soy were higher than in the plants grown in G soil. For wheat, the Ni concentrations were similar on both soils. Worth noting is that the G soil was more acidic than the M soil. The higher Ni concentrations in the biomass of the plants grown on the M soil cannot be explained by a lower pH and therefore a higher metal mobilization through higher acidity.

Typical Ni concentrations in plants on non-contaminated soils range from 0.05 to 5 mg/kg (Broadley et al., 2012). Our results are at the top end of this range. A sufficient supply of the plants with nickel as a micronutrient is in the range of 0.01 to 10 mg/kg. Potential Ni-toxicity starts with 10 mg/kg in Ni-sensitive plants and 50 mg/kg in moderately tolerable species (Broadley et al, 2012).

Spinach had the highest Ni-concentration of the measured plants which was to be expected because spinach has one of the highest transfer factors of heavy metals from soil to plant tissue (transfer factor = total conc. in plant/ total conc. in soil). Only fodder beet, lucerne and beans were found to have a higher transfer factor than spinach (Machelett et al., 1993).

Legumes have a higher Ni-demand than grasses. Also, the planting of legumes gradually declines the soils pH (Donald and Williams,1954). On fields and pastures, it takes from 25 to 50 years to drop the soil pH one unit (Lee, 1980), but in greenhouse conditions it might take much less time. This acidification of the soil may lead to higher mobility of Ni, which may have accounted for the higher Ni-concentration in the soy plants than the wheat plants. One explanation for the low Ni-concentrations in wheat could be that Ni is accumulated in the roots rather than in the shoots. Puschenreiter et al. (2017) found in the biomass of wheat plants, of a serpentine soil from Redlschlag Austria, higher Ni-concentrations in the roots than in the shoot. It cannot be derived from our data because the root concentration has not been measured.

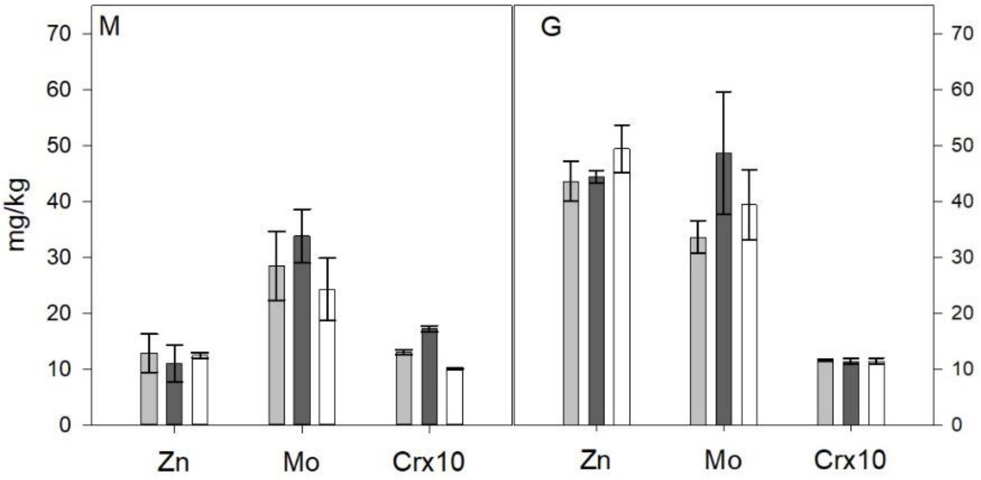

Figure 9 Concentration (in mg/kg) of zinc (Zn), molybdenum (Mo), and chromium (Cr) **in shoot biomass of soy, planted in M and G) soil**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The chromium concentrations were multiplied by 10 for better readability.

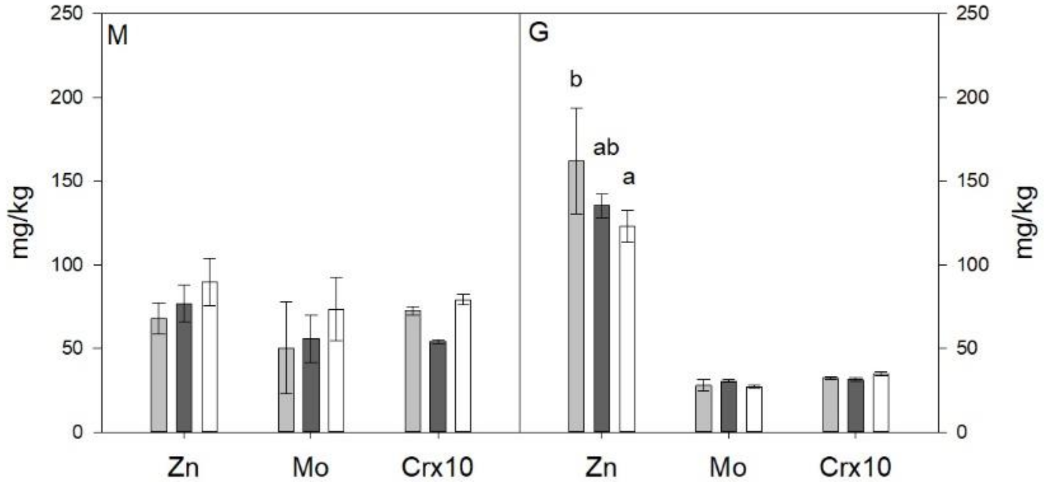

Figure 10 Concentration (in mg/kg) of zinc (Zn), molybdenum (Mo), and chromium (Cr) **in shoot biomass of spinach, planted in M and G soil**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The chromium concentrations were multiplied by 10 for better readability.

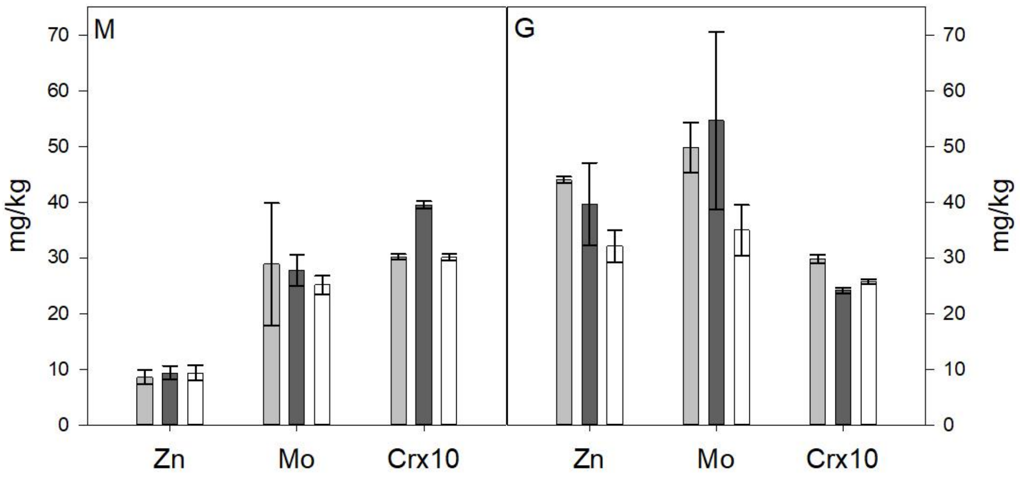

Figure 11 Concentration (in mg/kg) of zinc (Zn), molybdenum (Mo), and chromium (Cr) in **shoot biomass of wheat planted, in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The chromium concentrations were multiplied by 10 for better readability.

There was no significant difference in the Mo concentrations in the shoot biomass between the different crops or the two soils. There was a significant difference in the Zn uptake of all the plants between the M and G soil. In soy and wheat, the uptake of Zn was three times as high in the G soil than in the M soil. In spinach the difference was not quite as high, only a plus of 25% in the G soil, but also notably. The Zn concentrations in the M soil were around 55 mg/kg and in the G soil about 70 mg/kg. This difference cannot be the reason for a threefold concentration of Zn in soy and wheat in the G soil. Probably it is due to the higher acidity in the G soil. Zn is more soluble in acidic soil (Kabata-Pendias,2011). G is a sandy soil and Aman Deep Sharma and Malhi (2005) found in their study that sandy soils had less retention capacity for Cr and more of it comes into solution and therefore available for the plants. Our findings contradicted these findings. The biomass of all plants tested had slightly higher amounts of Cr in the silty-clay soil M.

Chromium had the highest concentrations in the spinach shoot biomass with about 4-8 mg/kg DM. Aman Deep Sharma and Malhi (2005) found that spinach retained most of the Cr in its non-edible root parts and transported lesser amounts to the edible leaf parts. In their experiment the leaf Cr concentration at an addition of 40 mg/kg Cr to the soil (similar to our experiment) was around 4 mg/kg DM, growing 40-90 days. Chromium is slightly available to plants and not easily translocated within plants, therefore it is concentrated mainly in roots, apparently because of the tendency of Cr^{3+} to bind to cell walls (Zayed et al.,1998).

The addition of B and BC did not have any significant effect on the Cr concentration in the plant shoot biomass. The controlling factor of Cr contents of plants are the soluble Cr contents of the soil. Most of the agricultural soils contain significant amounts of Cr, but the availability to plants is highly limited (Kabata-Pendias, 2011). The treatments with B and BC seem to not have had significantly changed the soluble Cr fractions and did not allow for more Cr to be taken up by the plants. In contrast to Kiekens and Camerlynck(1982) who found that the heavy metal accumulation in plants, after applying heavy metals to the soils, was lower on heavy clay soils than on sandy soils, our results showed that the plant accumulation was the same in both soils and even higher in the clayey M soil for Cr and Ni in soy and spinach.

Swoboda (2016), found in his Master thesis “Rock Dust as Agricultural Soil Amendment: A Review”, that it is very difficult to compare the different studies on stone meals as soil amendments, due to lack of consistency in terms of design and the factorial uniqueness of each trial. Also, the weathering of the rock material and thus its effectiveness is dependent on a lot of site-specific factors and interactions that at the moment are not completely understood. The studies all used different soils and stone meals, different applications quantities, and plants, which limits the comparison with the data presented in this thesis.

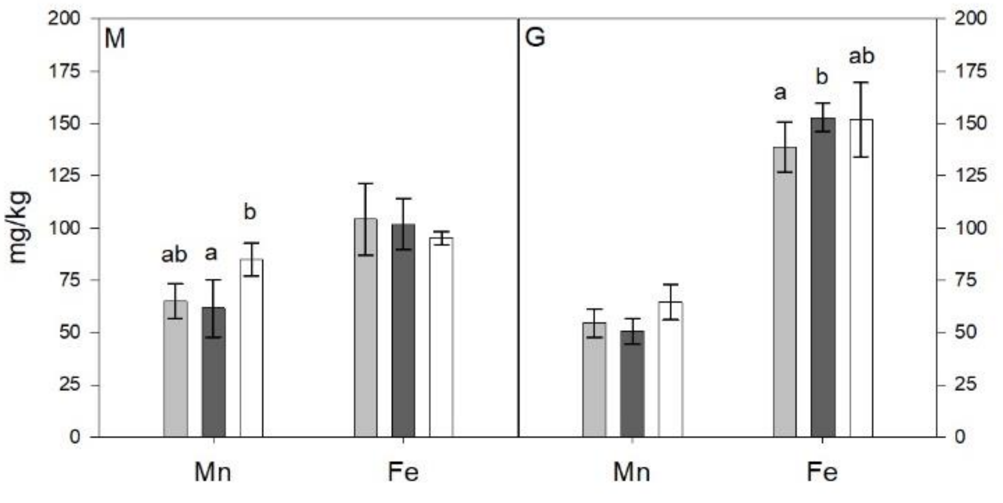

Figure 12 Elemental concentrations in mg/kg (manganese (Mn), iron (Fe)) in **shoot biomass of soy planted, in M and G soil.**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

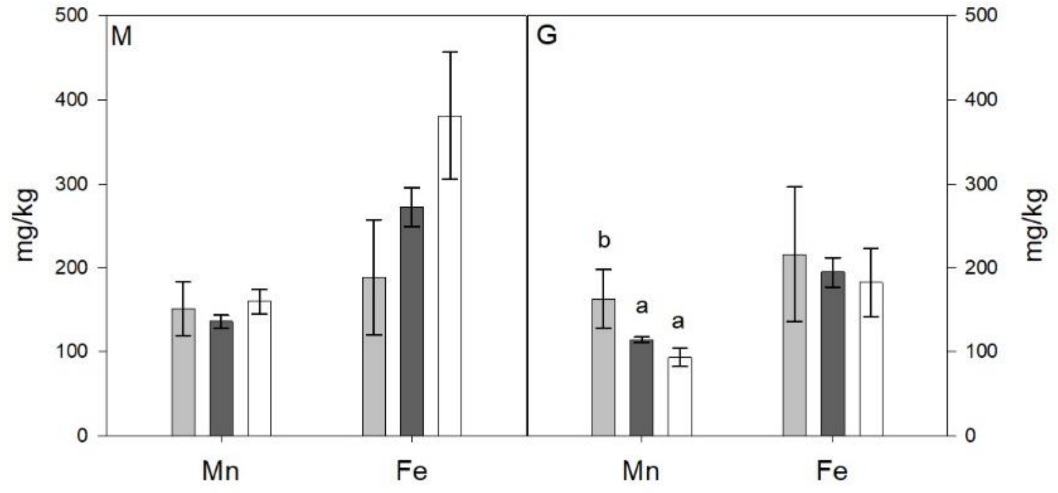

Figure 13 Elemental concentrations in mg/kg (manganese (Mn), iron (Fe)) in **shoot biomass of spinach, planted in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

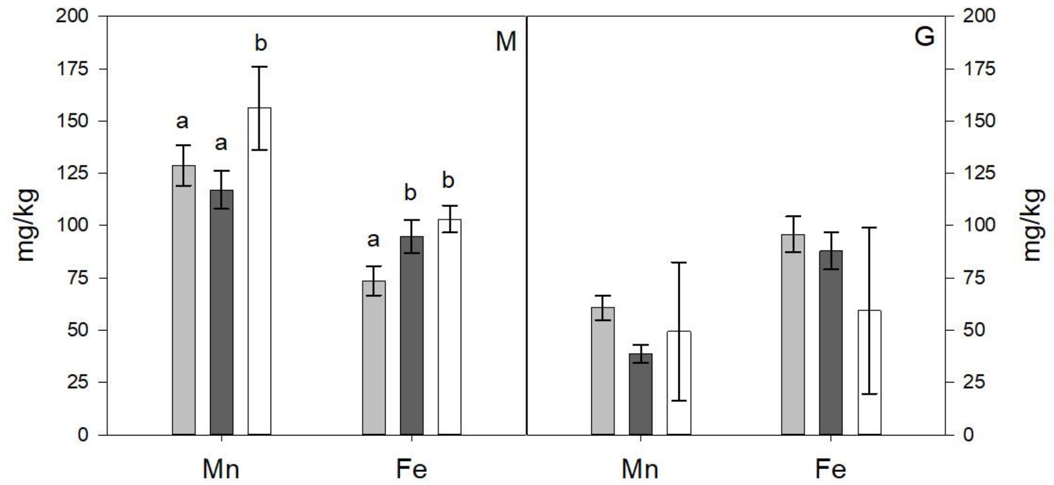

Figure 14 Elemental concentrations in mg/kg (manganese (Mn), iron (Fe) in **shoot biomass of wheat planted, in M and G soil.**:Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

In figure (12-14) manganese- and iron concentration of the shoot biomass are depicted. The B and BC treatments did not have a significantly positive effect on the uptake of Mn or Fe. Only the B treatment in spinach on the G soil had a significant effect on the uptake of Mn. Also, the trace elements Co, As and Pb were measured in the plant biomass but the concentrations were smaller than the LOQ and are presented in the annex.

3.4 Concentrations of macro-elements in shoot biomass

The addition of basalt stone meal can promote the accessibility of main nutrients (Snoek and Wülfrath,1995). Therefore, not only trace elements were measured but also the elements Ca, K, P, Mg. Al and Na also were measured. Na is not presented in this thesis because the concentrations were below the limit of quantification (LOQ).

The wheat biomass in both soils with the BC treatment showed a significant increase in phosphorus (figure 20). For the spinach biomass the effect was only significant for the M soil (figure 18). This effect was not discernible for the soy biomass other than that in the G soil the B treatment decreased the P concentration significantly. The B- and BC treatment had a significant effect on the Al concentration in the soy biomass (figure 16). Al gets more soluble in acidic soil (Kabata-Pendias, 2011). Since the Al concentrations were low, the pH was probably not under 4.5. Only the soy plants with the tendency to acidify the soil showed significant differences in the Al concentrations. In the M soil the K concentrations in all plants were higher in most B and BC treatment, but only significantly in the wheat BC treatment (figures 15,17,19). For Mg and Ca no effects were detected. A fertilization effect was only recognizable for P. If the basalt meal had lower Cr and Ni concentrations, it would be applicable in organic agriculture, where it would act as P fertilizer in addition to the improvement of the soil physical characteristics. Sayedahmed (1993) reported, that by adding 5 or 10 t of basalt stone meal per ha and year, a significant increase in Mg in barley shoot biomass was found in the second year of the trial but not after the first year of the experiment.

The K concentrations were significantly higher in the stone meal and compost treatment in the first year than the control. The P concentrations also increased significantly in the barley shoot biomass in the second year of the experiment. This indicates that more time is needed until different plant nutrients become available to the crops. In Central Europe, due to the pH values of the soils (usually > 5.5) and other general ecological conditions (temperature, precipitation), an improvement in the supply of plant nutrients through stone meal is not to be expected (AGES, 2015). In other climates this can be different. Shamshudin and Anda (2012) found in a field trial in Malaysia that a combined treatment of basalt stone meal and compost resulted in the highest values for soil exchangeable Mg and Ca, NPK values in cacao leaves, cacao hight and girth. The best results were obtained for 20 t/ha added compost and basalt stone meal rates of 5 and 10t/ha.

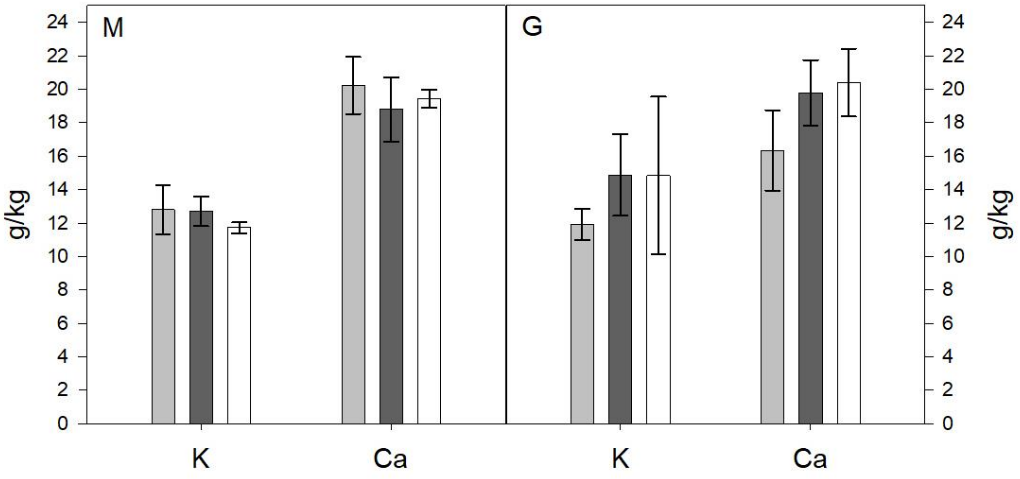

Figure 15 Concentration (in g/kg) of potassium (K) and calcium (Ca) in **shoot biomass of soy planted, in M and G soil**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

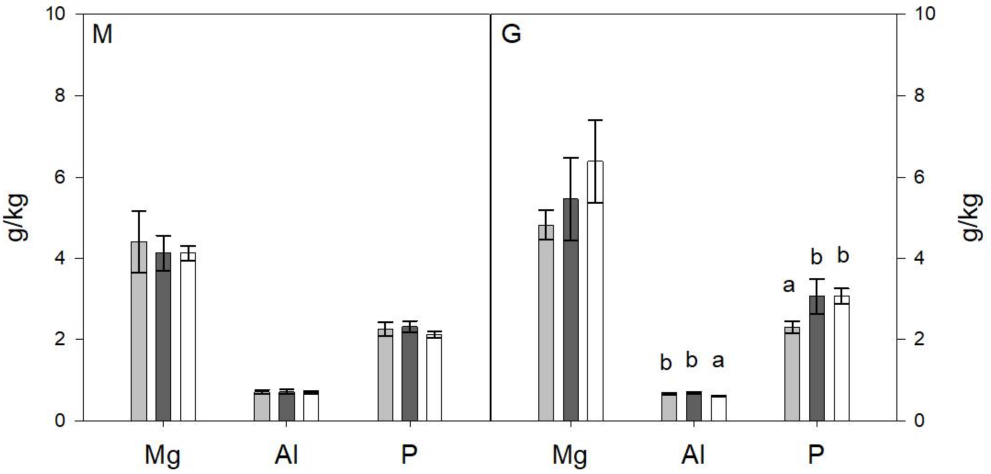

Figure 16 Concentration (in g/kg) of magnesium (Mg) and aluminium (Al) in **shoot biomass of soy, planted in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

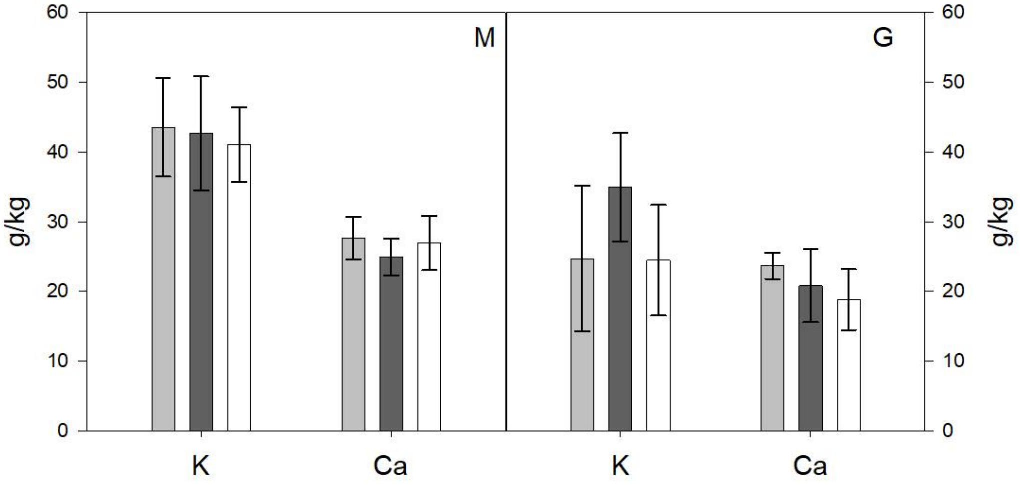

Figure 17 Concentration (in g/kg) of potassium (K) and calcium (Ca) in **shoot biomass of spinach, planted in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

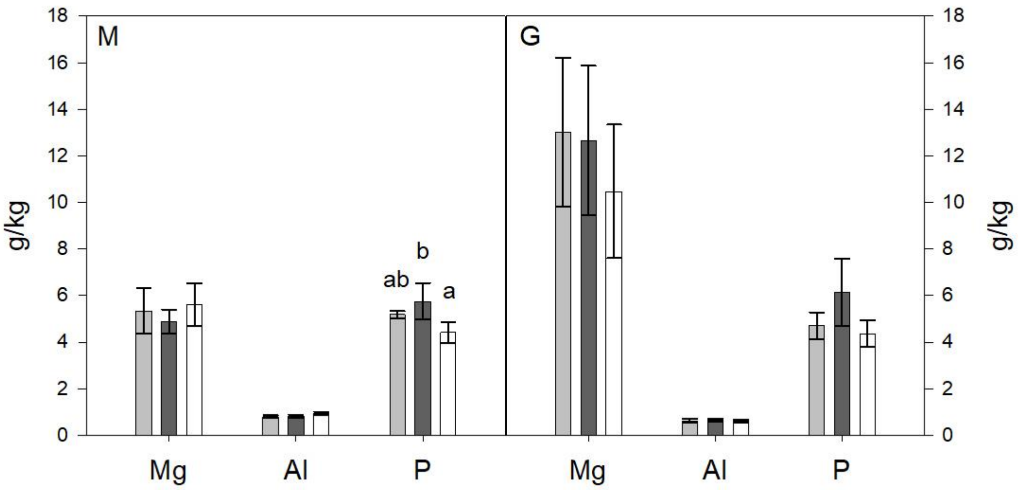

Figure 18 Concentration (in g/kg) of magnesium (Mg) and aluminium (Al) in **shoot biomass of spinach, planted in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

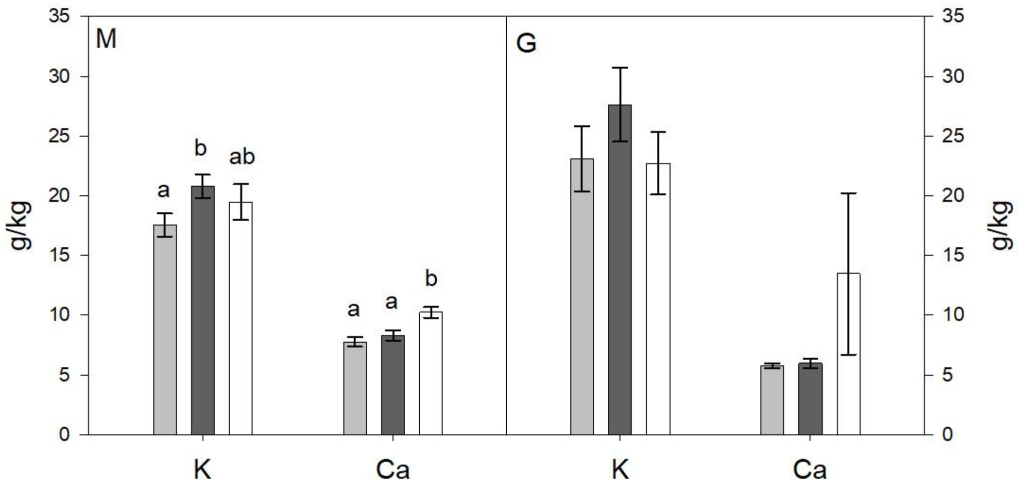

Figure 19 Concentration (in g/kg) of potassium (K) and calcium (Ca) in **shoot biomass of wheat, planted in in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, p < 0.05, ANOVA).

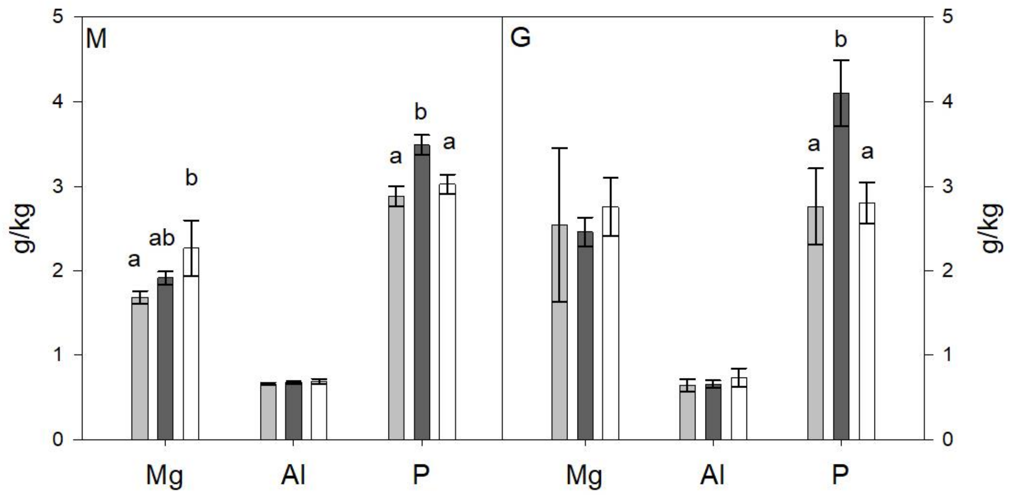

Figure 20 Concentration (in g/kg) of magnesium (Mg) and aluminium (Al) in **shoot biomass of wheat, planted in M and G soil.** Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, p < 0.05, ANOVA).

3.5 Concentration of Nickel and other elements (labile fractions) in the Ammonium-Nitrate-Extract of the Soil

The Ammonium-Nitrate-Extract can be used not only to predict the plant availability (labile fraction) of some metals but also their leaching risk. The data presented were determined in the Ammonium-Nitrate-Extract after plant harvesting. The data values (figures 21-27) show the impact of the different treatments B and BC on the extractability of metals in the soil. Further the chapter also reflects on the impact of plant growth and the associated depletion of the elements as a consequence of element uptake by roots.

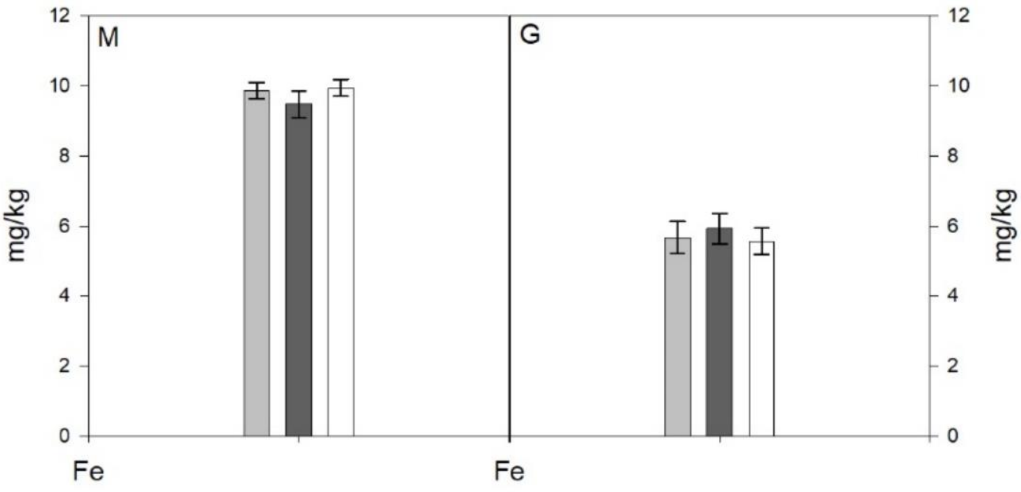

Figure 21 Concentration (in mg/kg) **of labile iron (Fe), in M and G soil not planted**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

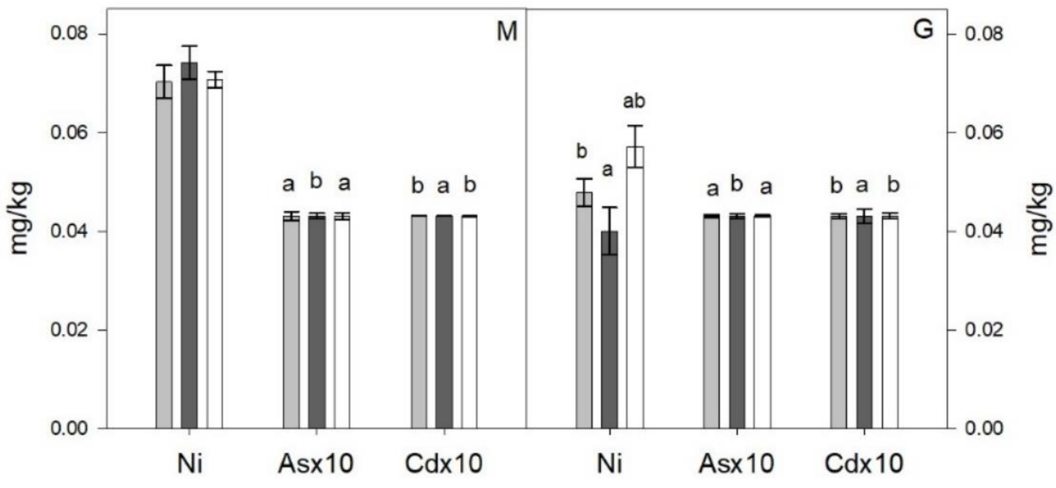

Figure 22 Concentration (in mg/kg) **of labile heavy metals** (nickel (Ni), arsenic (As), cadmium (CD)) **in M and G soil not planted**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The concentrations of arsenic and cadmium have been multiplied by 10 for better readability.

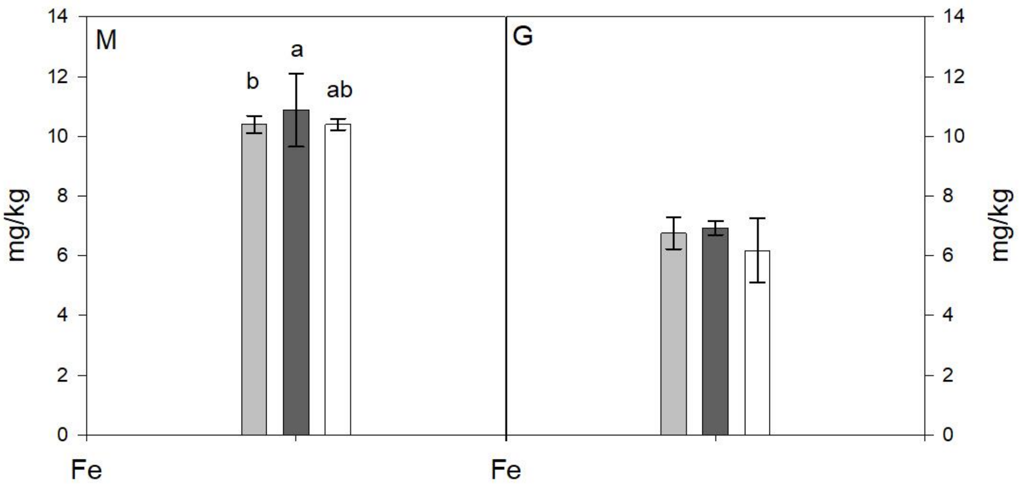

Figure 23 Concentration (in mg/kg) **of labile iron (Fe), in M and G soil planted with soy**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

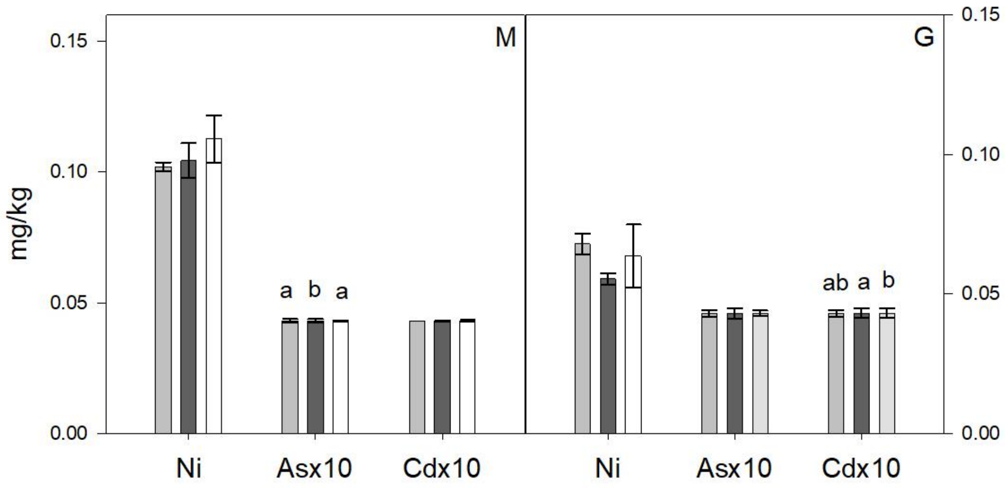

Figure 24 Concentration (in mg/kg) **of labile heavy metals** (nickel (Ni), arsenic (As), cadmium (Cd)) **in M and G soil planted with soy**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The concentrations of arsenic and cadmium have been multiplied by 10 for better readability.

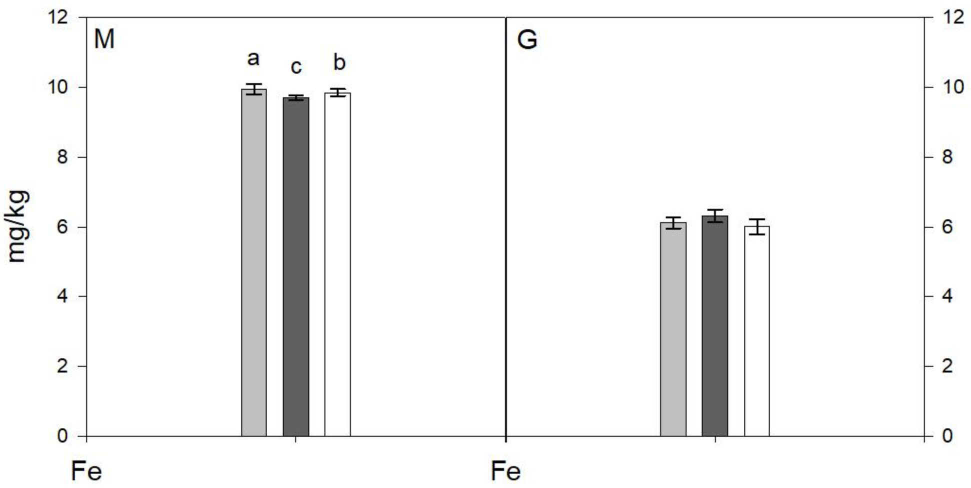

Figure 25 Concentration (in mg/kg) **of labile iron (Fe), in M und G soil planted with spinach**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

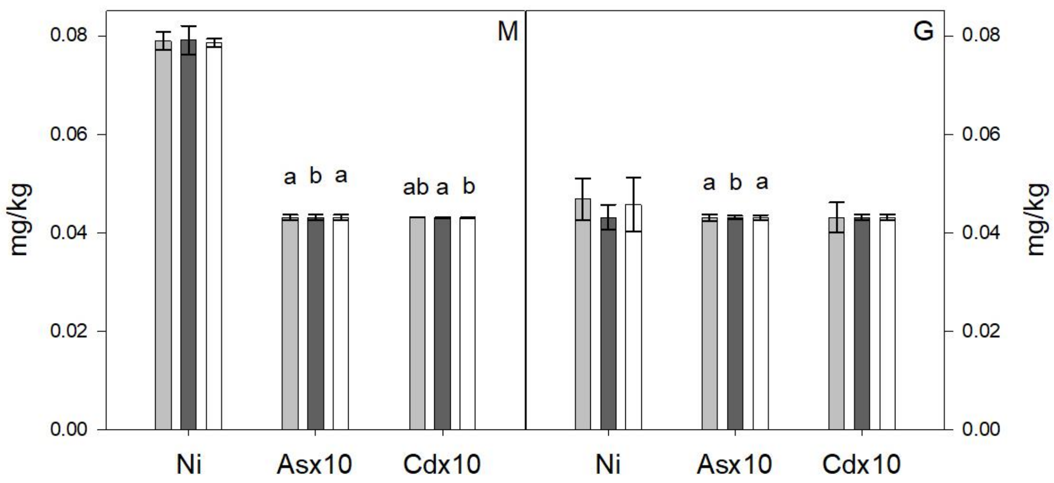

Figure 26 Concentration (in mg/kg) **of labile heavy metals** (nickel (Ni), arsenic (As), cadmium (Cd)) **in M and G soil planted with spinach**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The concentrations of arsenic and cadmium have been multiplied by 10 for better readability.

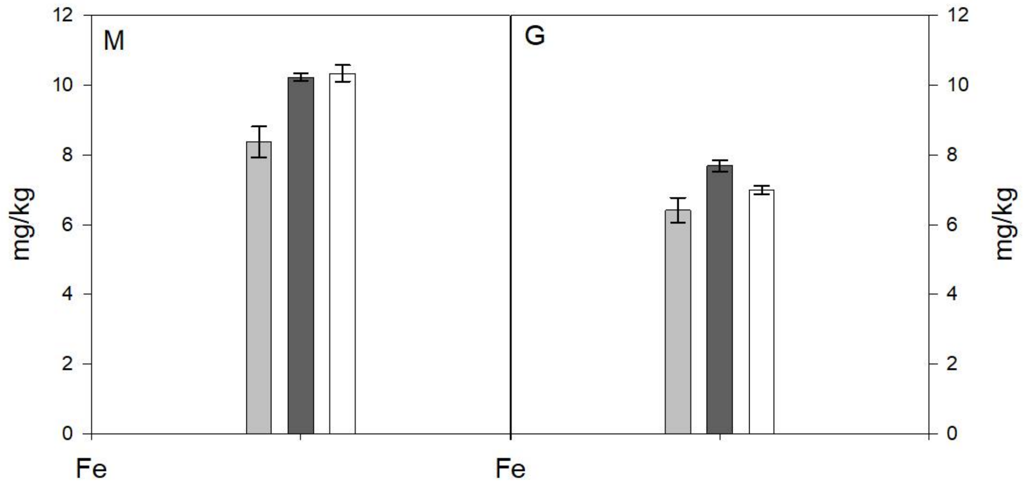

Figure 27 Concentration (in mg/kg) **of labile iron (Fe), in M and G soil planted with wheat**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA).

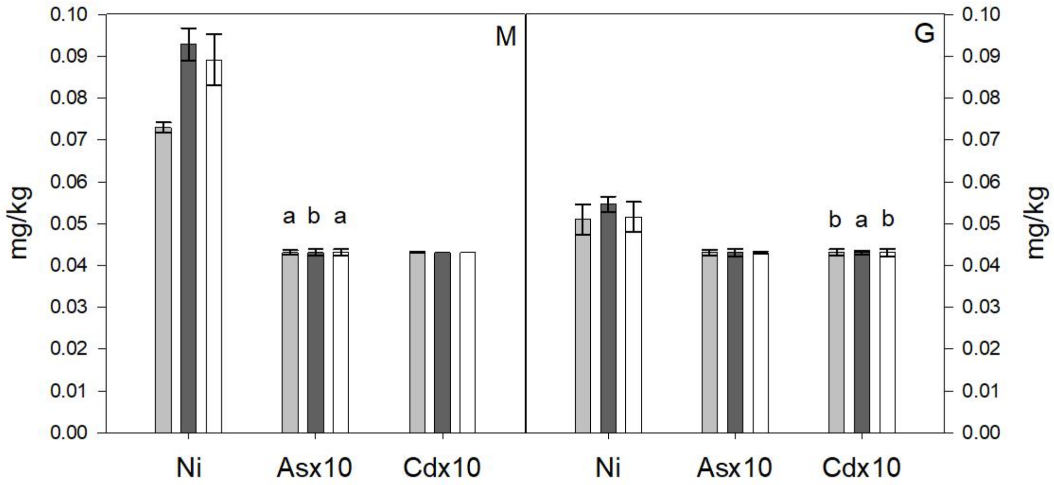

Figure 28 Concentration (in mg/kg) **of labile heavy metals** (nickel (Ni), arsenic (As), cadmium (Cd)) **in M and G soil planted with wheat**. Treatments: Basalt stone meal (light grey bar), Basalt stone meal+ Compost (dark grey bar) and no treatment (white bar). Error bars indicate the standard error of the mean, different letters indicate significant differences between the treatments (n=4, $p < 0.05$, ANOVA). The concentrations of arsenic and cadmium have been multiplied by 10 for better readability.

Besides the availability for plants, the leaching behaviour can also be predicted. The Ammonium-nitrate extractable element concentrations were determined after the completion of the pot experiment. The concentrations therefore represent both, the influence of the different treatments, and of plant growth and the associated depletion of elements through absorption by the roots. The solubility of Ni in unplanted soils did not significantly change with different treatments. There was a slight increase in Ni in the M soil and a slight but significant decrease in Ni in the G soil connected to the B and BC treatment. This could be connected to a change in the pH of the soils. The changes in As and Cd were marginal and not remarkable. The soil in planted pots also did show no significant changes in labile Ni, As, or Cd through the different treatments. Even the different plants did not have a significant effect on the labile Ni or Fe concentrations of the two soils. The M soil had about 0.09 mg/kg labile Ni and about 10 mg/kg of labile Fe in all the pots whether they were planted or not. The G soil had about 0.05 mg/kg of labile Ni and about 6.5 mg/kg of labile Fe. These results were interesting because the G soil had a lower pH and therefore should mobilize more metals in the soil, but in our experiment the M soil had more mobile metals. Worth mentioning is that the total Fe content in the G soil is about 5 g/kg higher than in the M soil. There was a higher concentration of labile Fe in the M soil, this could be due to the different textures and pHs of the soil. The G soil was coarser but had a lower pH. The concentration of labile Ni in the M soil was higher even though the total Ni concentrations were the same in M and G. Maybe the same attribute that promoted the solubility of Fe in M was also responsible for Ni.

Besides Ni, As, and Cd also Zn, Cu, Mo, Pb and Mn were measured, but all the results were under the LOQ.

Chromium was not measured in the Ammonium-Nitrate extract because this extract is only partially suitable for measuring labile Cr. In past measurements the Cr concentrations were under the LOD most of the time. The available data is also consistent with the findings of Scheidl (2015), where nickel and other elements were hardly released in the eluates of the basalt stone meal.

In Austria there is an OENORM (2000) in place for contaminated soils, called use-specific assessment of the contamination of soil from old sites and old deposits. This OENORM (2000) states limit values for Ammonium-Nitrate extractable concentrations of heavy metals in soils. The limit value for plant toxicity is 1 mg/kg Ni for impairment of plant growth. There is no limit value for Ni to impair the quality of livestock feed or food for humans. The concentrations were in the experimental soils more than 10 times lower and there was no indication that the addition of basalt stone meal or basalt stone meal + compost changed that. The limit values for As are 0.1 mg/kg to impair food and feed quality and 0.6 mg/kg to impair plant growth. The concentrations in the experimental soils were way lower than those limit values. For Cd the limit value is 0.04 mg/kg to impair food and feed quality but no limit value for plant toxicity is given.

4 Conclusion

The investigated basalt stone meal shows increased concentrations of nickel and chromium, which could lead to a release of these elements into the environment, after use as soil additive or as additive for composting, via weathering processes. This could lead to an accumulation of Ni and Cr in the soil and the plants growing in the soil. In this experiment basalt stone meal, and a basalt stone meal-compost mixture were added to two different soils planted with three different crops (wheat, spinach, and soy). The plants all had different element mobilization mechanisms. There were slight increases in Ni and Cr and P in the plants. However, P was mostly released from the compost. The changes of the labile Ni and Cr concentrations in the soils through the two different treatments and the different plantings were negligible. The addition of basalt stone meal as a soil additive or in composting is harmless with regard to the possible release of nickel or chromium. Positive effects in terms of nutrient supply have only been observed to a very small extent. A fertilization effect was only recognizable for P. If the basalt meal had lower Cr and Ni concentrations, it would be applicable in organic agriculture, where it would act as P fertilizer in addition to the improvement of the soil physical characteristics. To summarize and answer the research question: there were no significant amounts of Ni or Cr released from the basalt stone meal from Pauliberg by using an agricultural conventional amount of stone meal. The different crops planted resulted in no significant difference in Ni and Cr release and plant uptake, and also the addition of compost did not increase the release of Ni and Cr in the soil or the plant uptake. Even though this experiment showed that no significant amounts of Ni and Cr were released into the soil a experiment over a longer period of time could lead to different results because different factors (weathering, acidification by root excudates,…) had very limited time in this experiment and this processes take time in Central European climate.

There were not many scientific studies in the past years in Europe about agricultural application of stone meal. Most of the more recent studies are form tropical regions with highly weathered soils and the comparability is hardly given. The more recent literature in Europe focuses on CO_2 sequestration. Earlier studies are very different in their methods and the results about the positive effects of stone meal application on agricultural soils.

For this experiment the pH values of the soils might have been interesting, to see the changes in acidity due to the different treatments and plants. Also, with regard for the human customer, the concentrations of Ni and Cr in the beans of the soy plants and the grains of the wheat plants would be of interest. Some studies found higher concentrations of Ni and Cr the plant roots and the shoots. To measure the root concentrations could be of interest to see how much Ni and Cr are taken out of the field and how much stays in the ground with the accumulation in the roots. For the next experiment with basalt stone meal from Pauliberg, a field experiment over one ore two years would be recommended, to see the potential accumulation of Ni and Cr in the soil and plants over a longer period of time and to see how strong Ni and Cr are bound in the basalt stone meal and soil. In this pot experiment 5 t/ha basalt stone meal (5.3 t in the stone meal +compost mixture) were added. In the field experiment also the application of higher amounts would be interesting, since more significant effects, positive and negative, cannot be ruled out. In literature the best results in biomass yields were accomplished with a mixture of compost and stone meal, or stone meal and NPK fertilizers. These combinations should be included in the field experiment. One more interesting aspect would be if the Cr and Ni concentrations in all locations of the quarry are continuously this high, or whether there are fluctuations in the concentrations. Maybe the Ni and Cr concentrations are way lower in some portions of the basalt stone from Pauliberg and could be used as a soil additive to agricultural soils.

Even though it would take over 170 years to reach the limit value of Ni and Cr in the soil by adding 5 t/ha per year basalt stone meal from Pauliberg, the use as soil amendment is legally not permitted because the tested stone meal itself had a too high concentration of Ni and Cr to be permitted under the fertilizer regulation. One possible use of the basalt stone meal from Pauliberg is as an additive to compost. There are no limit values on heavy metal concentrations in stone meals, and as legally only 5 mass percent of stone meal can be added, the limit value of 100 mg/kg Ni and 250 mg/kg Cr in the end product are not easily exceeded.

For the future, like Swoboda (2016) said, cooperation between scientists and farmers as well as expertise in both biology and mineralogy is needed to evaluate the practicality of stone meal and to fully understand weathering mechanisms. The stone meals have to be tested over a longer period of time in field experiments. Even though such trials would require substantial investment in terms of time and resources, it would grant real insight in what ameliorative effects stone meals really have. Most potential for the future use is seen in CO_2 sequestration combined with the other positive effects stone meal can have, as they are readily available in high quantities. The ongoing depletion of soil nutrients is one of the main reasons for global food insecurity. In combination with growing concerns about the current fertilizer situation it justifies further examinations and investments in this field.

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8 Annex

Calculation to reach the limit value

Nickel:

Moosbierbaum

Possibel addition of Ni: 100mg/kg limit value – 22.9 mg/kg Ni in M soil = 77.1 mg kg-1

Additon of basalt stone meal: 5 t/ha = 1.79 g kg-1

Ni concentration stone meal: 334 mg kg-1 -. µg g-1 —> 334 * 1.79 = 598 µg Ni per kg and year

Possibel Ni additon: 77100 / 598 = 129 years

Gföhl

Possibel addition of Ni: 100mg/kg limit value – 21.7 mg/kg Ni in G soil = 78.3 mg kg-1

Additon of basalt stone meal: 5 t/ha = 1.79 g kg-1

Ni concentration stone meal: 334 mg kg-1 -. µg g-1 —> 334 * 1.79 = 598 µg Ni per kg and year

Possibel Ni additon: 78300 / 598 = 129 years

Chromium:

Moosbierbaum

Possibel addition of Ni: 100mg/kg limit value – 39 mg/kg Cr in M soil = 61 mg kg-1

Additon of basalt stone meal: 5 t/ha = 1.79 g kg-1

Cr concentration stone meal: 191 mg kg-1 -. µg g-1 —> 191 * 1.79 = 341.9 µg Cr per kg and year

Possible Cr additon: 61000 / 341.9 = 178 years

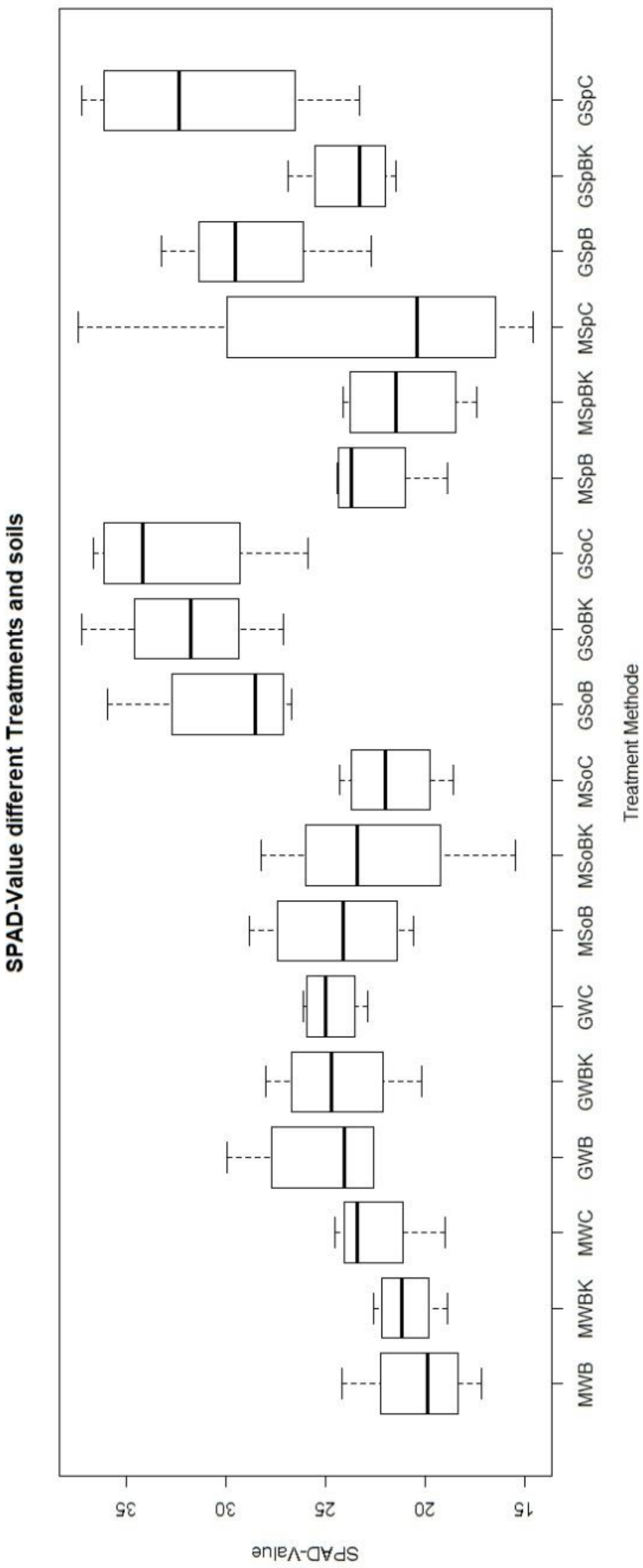
Gföhl

Possibel addition of Ni: 100mg/kg limit value – 42.9 mg/kg Cr in M soil = 57.1 mg kg-1

Additon of basalt stone meal: 5 t/ha = 1.79 g kg-1

Cr concentration stone meal: 191 mg kg-1 -. µg g-1 —> 191 * 1.79 = 341.9 µg Cr per kg and year

Possible Cr additon: 57100 / 341.9 = 167 years



SPAD-Value different Treatments and soils
SPAD-Value
15
20
25
30
35
MWB
MWBK
MWC
GWB
GWBK
GWC
MSoB
MSoBK
MSoC
GSoB
GSoBK
GSoC
MSpB
MSpBK
MSpC
GSpB
GSpBK
GSpC
Treatment Methode

Spand Value/ Shoots and Biomass

Number	Soil Type	Type of Plant	Configuratio	Replication	SPAD Value	Number of s	Biomass (g)
1	M	W	B	1	24.2	15	1.889
2	M	W	B	2	20.3	10	1.755
3	M	W	B	3	19.5	9	1.689
4	M	W	B	4	17.2	10	1.759
5	M	W	BC	1	21.7	10	1.67
6	M	W	BC	2	20.7	15	1.822
7	M	W	BC	3	18.9	10	1.303
8	M	W	BC	4	22.6	11	1.286
9	M	W	NT	1	19	10	1.838
10	M	W	NT	2	24.5	12	1.851
11	M	W	NT	3	23.6	8	1.745
12	M	W	NT	4	23.2	11	1.512
13	M	So	B	1	26	4	2.282
14	M	So	B	2	22.2	4	2.819
15	M	So	B	3	28.8	4	3.594
16	M	So	B	4	20.6	4	3.208
17	M	So	BC	1	23.8	3	3.776
18	M	So	BC	2	23	5	2.487
19	M	So	BC	3	15.5	4	2.948
20	M	So	BC	4	28.2	5	2.424
21	M	So	NT	1	18.6	3	2.836
22	M	So	NT	2	24.3	6	4.614
23	M	So	NT	3	20.9	4	2.277
24	M	So	NT	4	23.1	5	3.197
25	M	Sp	B	1	24.4	3	0.401
26	M	Sp	B	2	18.9	4	0.58
27	M	Sp	B	3	24.3	5	0.549
28	M	Sp	B	4	23.1	3	0.392
29	M	Sp	BC	1	19.5	10	0.592
30	M	Sp	BC	2	23.4	4	0.408
31	M	Sp	BC	3	17.4	9	0.692
32	M	Sp	BC	4	24.1	8	0.503
33	M	Sp	NT	1	14.6	4	0.344
34	M	Sp	NT	2	22.4	4	0.233
35	M	Sp	NT	3	37.4	4	0.625
36	M	Sp	NT	4	18.4	8	0.494
37	G	W	B	1	22.6	9	2.753
38	G	W	B	2	25.5	8	2.461
39	G	W	B	3	29.9	8	2.737
40	G	W	B	4	22.6	9	3.081
41	G	W	BC	1	28	8	2.574
42	G	W	BC	2	24	7	2.4
43	G	W	BC	3	20.2	8	2.566
44	G	W	BC	4	25.4	8	2.745
45	G	W	NT	1	26.1	8	2.636
46	G	W	NT	2	25.8	7	2.382
47	G	W	NT	3	24.2	9	2.63
48	G	W	NT	4	22.9	9	2.812
49	G	So	B	1	27.5	3	4.049
50	G	So	B	2	29.5	4	3.48
51	G	So	B	3	26.7	4	4.274
52	G	So	B	4	35.9	4	4.639
53	G	So	BC	1	37.2	4	5.116
54	G	So	BC	2	31.6	4	4.664
55	G	So	BC	3	31.9	4	2.979
56	G	So	BC	4	27.1	4	4.228
57	G	So	NT	1	36.6	5	5.026
58	G	So	NT	2	35.6	4	4.738
59	G	So	NT	3	32.7	5	4.501
60	G	So	NT	4	25.9	3	4.624
61	G	Sp	B	1	29.5	4	1.311
62	G	Sp	B	2	22.7	4	1.118
63	G	Sp	B	3	29.5	4	1.167
64	G	Sp	B	4	33.2	4	1.441
65	G	Sp	BC	1	24.1	4	1.338
66	G	Sp	BC	2	21.5	5	1.572
67	G	Sp	BC	3	26.9	3	1.334
68	G	Sp	BC	4	22.5	5	1.484
69	G	Sp	NT	1	35	4	1.228
70	G	Sp	NT	2	23.3	5	1.512
71	G	Sp	NT	3	29.7	4	1.033
72	G	Sp	NT	4	37.2	4	1.168

ICP-MS Plant digest

	mg kg-1 **Mn**	mg kg-1 **Fe**	mg kg-1 **Co**	mg kg-1 **Ni**	mg kg-1 **Cu**	mg kg-1 **Zn**	mg kg-1 **As**	mg kg-1 **Mo**	mg kg-1 **Cd**	mg kg-1 **Pb**
MWB	128.787	73.597	-0.018	2.693	4.349	8.557	0.144	23.389	0.169	-0.008
MWBK	117.050	94.738	0.006	3.956	4.804	9.324	0.163	27.728	0.124	0.259
MWC	156.105	103.114	-0.002	2.645	4.573	9.341	0.194	25.101	0.228	0.144
MSOB	64.948	104.243	0.084	5.336	6.975	12.863	0.054	28.509	0.100	0.144
MSOBK	61.653	101.816	0.081	5.266	6.406	10.998	0.073	33.814	0.094	-0.043
MSOC	84.867	95.243	0.079	4.408	6.546	12.455	0.033	24.300	0.101	0.061
MSPB	151.268	188.958	1.274	7.332	9.355	67.917	0.186	50.354	0.911	0.195
MSPBK	136.138	272.259	1.288	6.113	10.785	76.736	0.204	55.722	0.674	0.294
MSPC	159.904	381.349	1.480	8.349	10.536	89.621	0.255	73.469	0.794	0.237
GWB	60.691	95.736	-0.046	2.938	5.921	43.954	0.099	49.822	0.172	0.564
GWBK	38.795	87.892	-0.048	2.655	6.505	39.606	0.118	60.715	0.148	0.305
GWC	49.370	59.357	-0.020	2.936	4.507	32.085	0.152	34.927	0.169	0.161
GSOB	54.508	138.812	0.035	2.764	6.570	43.648	0.042	33.624	0.179	0.125
GSOBK	50.523	136.167	0.043	2.353	7.452	44.432	0.033	48.720	0.106	0.218
GSOC	64.577	151.890	0.049	2.665	7.064	49.473	0.029	39.437	0.160	0.124
GSPB	162.999	216.219	0.390	3.828	11.284	180.691	0.102	27.927	2.387	0.050
GSPBK	114.204	194.720	0.370	3.887	11.064	135.203	0.074	30.501	1.614	0.387
GSPC	93.450	182.717	0.268	4.275	9.168	123.064	0.072	27.121	1.736	0.157
Compost	490	15867	6.448	21.023	22.966	103.643	8.159	10.545	0.237	12.367

ICP MS Ammonium Nitrat Extract

	Fe	Ni	As	Cd	Zn	Cu	Mo	Pb	Mn
	57	60	75	114	64	63	98	208	55
	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1	mg kg-1
MWB	8.379	0.073	0.004	0.001	0.020	0.055	0.001	-0.002	0.109
MWBK	10.236	0.093	0.007	0.001	0.033	0.078	0.004	-0.001	0.156
MWC	10.346	0.089	0.005	0.001	0.025	0.067	0.003	-0.001	0.199
MSOB	10.403	0.102	0.006	0.001	0.022	0.099	0.002	-0.002	0.159
MSOBK	10.882	0.104	0.008	0.001	0.023	0.103	0.003	0.000	0.148
MSOC	10.402	0.113	0.006	0.001	0.023	0.114	0.004	-0.002	0.249
MSPB	9.958	0.079	0.005	0.000	0.013	0.037	0.001	-0.002	-0.016
MSPBK	9.715	0.079	0.007	0.000	0.013	0.041	0.001	-0.003	-0.018
MSPC	9.858	0.079	0.005	0.000	0.012	0.043	0.001	-0.003	-0.018
GWB	6.420	0.051	0.003	0.003	0.023	0.025	0.000	-0.002	0.815
GWBK	7.692	0.055	0.005	0.002	0.011	0.048	0.001	-0.002	0.735
GWC	7.007	0.052	0.003	0.004	0.030	0.023	0.000	-0.001	2.342
GSOB	6.765	0.068	0.003	0.008	0.104	0.029	0.000	0.000	4.297
GSOBK	6.936	0.055	0.004	0.003	0.026	0.042	-0.001	-0.001	1.739
GSOC	6.180	0.064	0.003	0.007	0.093	0.030	-0.001	0.000	4.999
GSPB	6.125	0.047	0.002	0.003	0.018	0.015	-0.004	-0.001	0.192
GSPBK	6.319	0.043	0.003	0.002	-0.009	0.020	-0.004	-0.002	0.018
GSPC	6.015	0.046	0.002	0.003	0.019	0.014	-0.005	0.000	0.180
MB	9.875	0.070	0.005	0.000	-0.024	0.037	-0.003	-0.003	-0.021
MBK	9.486	0.074	0.007	0.000	-0.026	0.041	-0.003	-0.003	-0.018
MC	9.952	0.071	0.005	0.000	-0.016	0.036	-0.003	-0.002	-0.020
GB	5.676	0.048	0.002	0.004	0.067	0.010	-0.004	-0.001	0.241
GBK	5.930	0.040	0.004	0.001	-0.016	0.019	-0.004	-0.002	0.023
GC	5.570	0.043	0.002	0.003	0.047	0.011	-0.005	-0.001	0.086

ICP OES Aqua Regia								
g/kg	K 766	Mg 285	Na 589	P 214	K 766	Mg 285	Na 589	P 214
MB	3.978	9.846	0.510	0.789	0.133	0.044	0.004	0.006
GF	3.947	5.221	0.500	0.577	0.032	0.200	0.010	0.010
MB_B	4.128	11.088	0.527	0.787	0.093	1.443	0.003	0.009
GF_B	3.956	5.249	0.504	0.585	0.093	0.217	0.008	0.007
MB_BK	4.202	10.080	0.551	0.852	0.283	0.679	0.009	0.076
GF_BK	4.535	5.945	0.536	0.680	1.234	1.044	0.069	0.081

ICP-MS Aqua Regia									
mg/kg	**Mg 24**	**Cr 52**	**Cr 53**	**Mn 55**	**Fe 57**	**Ni 58**	**Co 59**	**Ni 60**	**Cu 63**
Ref_AQ_1	2378.400	38.291	41.101	521.045	11399.121	113.840	6.129	17.596	9.075
Ref_AQ_2	2250.934	32.927	17.834	501.190	10992.636	110.905	5.911	16.928	8.847
Ref_AQ_3	2464.791	38.642	40.998	534.317	11775.900	116.349	6.176	17.533	9.039
MB_1	9437.035	32.054	39.886	567.486	17112.652	166.697	8.642	23.196	15.399
MB_2	9169.493	32.192	38.078	557.467	16914.055	162.851	8.521	22.551	14.463
MB_B_1	11792.169	31.684	40.460	554.889	16777.331	162.363	8.503	22.782	14.207
MB_B_2	9580.867	33.644	42.774	571.850	17410.882	167.568	8.766	23.569	15.573
MB_BK_1	9289.761	33.444	39.789	550.768	17054.761	164.627	8.595	23.099	14.603
MB_BK_2	9132.448	32.795	39.629	556.363	16952.013	163.312	8.629	22.897	14.568
Gf_1	4592.544	41.938	46.958	805.499	21259.005	200.320	14.124	22.228	16.693
Gf_2	4393.181	39.846	38.977	740.605	19390.759	183.280	13.343	21.114	16.151
Gf_B_1	4492.366	40.712	39.828	735.998	19748.892	186.749	13.651	21.584	16.009
Gf_B_2	4367.525	41.657	47.797	746.464	20646.904	194.643	14.388	22.558	21.803
Gf_BK_1	4864.673	44.612	50.584	798.102	21667.030	203.201	14.623	23.175	17.803
Gf_BK_2	4151.364	36.575	26.426	691.032	18641.573	178.211	13.403	20.751	21.261

ICP-MS Aqua Regia									
mg/kg	**Zn 64**	**Cu 65**	**Zn 66**	**Zn 68**	**As 75**	**Cd 111**	**Cd 114**	**Pb 207**	**Pb-1 208**
Ref_AQ_1	41.246	9.089	38.598	37.651	4.756	0.122	0.131	12.179	13.049
Ref_AQ_2	38.583	8.760	37.327	36.745	2.591	0.143	0.134	12.180	13.033
Ref_AQ_3	42.069	9.153	39.159	38.712	5.102	0.130	0.128	12.754	13.597
MB_1	55.207	15.618	46.716	45.538	9.365	0.190	0.195	12.583	13.310
MB_2	54.406	14.720	46.278	45.377	8.657	0.189	0.179	12.838	13.684
MB_B_1	54.508	14.520	46.631	45.097	8.964	0.178	0.188	12.971	13.804
MB_B_2	56.137	15.780	47.614	47.187	9.180	0.188	0.207	13.804	14.846
MB_BK_1	54.090	14.855	46.510	45.654	9.047	0.184	0.177	12.741	13.609
MB_BK_2	56.267	14.878	47.642	47.000	9.255	0.177	0.186	12.603	13.471
Gf_1	71.588	17.253	57.651	55.118	3.116	0.200	0.209	11.901	12.808
Gf_2	68.224	16.532	54.933	53.416	2.581	0.219	0.207	11.154	12.007
Gf_B_1	69.020	16.375	56.941	55.197	2.313	0.211	0.205	11.685	12.578
Gf_B_2	67.630	22.015	54.707	52.849	3.364	0.207	0.208	11.426	12.449
Gf_BK_1	76.069	18.502	60.138	57.715	3.398	0.207	0.206	12.501	13.463
Gf_BK_2	66.510	21.561	57.864	56.357	1.042	0.216	0.219	12.117	13.040

ICP OES Aqua Regia						
	K 766	Na 589	P 214	F 259	Ca 315	Al 396
MB_1	3.89	0.52	0.84	17.483	24.742	16.249
MB_2	4.08	0.51	0.84	17.458	24.854	16.671
MB_B_1	4.07	0.54	0.83	14.139	23.682	13.158
MB_B_2	4.20	0.53	0.84	17.085	24.230	15.911
MB_BK_1	4.41	0.57	0.96	18.078	26.424	16.915
MB_BK_2	4.01	0.55	0.85	17.085	24.158	16.293
Gf_1	3.98	0.50	0.62	23.277	3.117	17.397
Gf_2	3.93	0.51	0.64	21.133	2.899	16.011
Gf_B_1	3.90	0.51	0.64	21.320	2.822	15.820
Gf_B_2	4.03	0.52	0.63	22.251	2.958	16.442
Gf_BK_1	5.42	0.59	0.79	23.077	3.534	12.830
GF_BK_2	3.67	0.49	0.67	21.852	2.943	14.926

ICP OES Plant digest						
mg/kg	P	Mg	K	Fe	Ca	Al
MWB1	2.809	1.268	16.718	-0.477	7.156	0.683
MWB2	2.749	1.218	16.762	-0.463	7.987	0.625
MWB3	2.947	1.400	18.158	-0.475	7.867	0.710
MWB4	3.009	1.288	18.598	-0.459	8.083	0.678
MWBK1	3.202	1.320	19.769	-0.441	7.400	0.684
MWBK2	3.272	1.592	20.673	-0.463	8.380	0.637
MWBK3	3.721	1.395	22.495	-0.467	8.789	0.709
MWBK4	3.762	1.947	20.236	-0.428	8.682	0.700
MWC1	2.921	2.038	17.648	-0.457	9.616	0.654
MWC2	3.071	1.547	21.284	-0.431	28.132	0.640
MWC3	3.166	2.384	20.541	-0.432	10.403	0.658
MWC4	2.949	1.679	18.502	-0.465	10.672	0.665
MSoB1	2.464	1.486	13.637	-0.500	22.419	0.675
MSoB2	2.185	4.470	11.696	-0.469	20.748	0.663
MSoB3	2.328	4.544	14.439	-0.472	18.814	0.726
MSoB4	2.053	3.211	11.439	-0.456	18.953	0.679
MSoBK1	2.434	3.972	13.546	-0.470	19.097	0.642
MSoBK2	2.128	3.951	11.466	-0.493	16.220	0.653
MSoBK3	2.341	3.094	12.781	-0.505	18.976	0.740
MSoBK4	2.381	4.024	13.060	-0.482	20.868	0.681
MSoC1	2.216	4.055	11.722	-0.503	19.267	0.680
MSoC2	2.100	3.682	11.843	-0.492	19.753	0.756
MSoC3	2.131	3.649	11.230	-0.486	20.094	0.660
MSoC4	2.029	3.576	12.113	-0.490	18.672	0.757
MSpB1	5.259	3.639	54.025	-0.384	26.139	0.679
MSpB2	5.202	5.962	39.634	-0.336	32.067	0.774
MSpB3	5.302	5.816	41.862	-0.379	25.140	0.655
MSpB4	4.970	5.088	38.846	-0.401	27.200	0.670
MSpBK1	4.770	4.569	37.410	-0.284	26.307	0.759
MSpBK2	6.688	5.472	54.673	-0.380	21.770	0.643
MSpBK3	5.791	4.238	37.456	-0.419	24.040	0.729
MSpBK4	5.733	4.568	41.161	-0.293	27.775	0.730
MSpC1	3.796	5.616	47.040	-0.325	28.983	0.688
MSpC2	4.579	6.549	38.394	-0.114	31.293	0.772
MSpC3	4.853	5.080	43.690	-0.240	22.607	0.873
MSpC4	4.405	4.267	35.069	-0.192	25.027	0.802
GWB1	2.857	1.830	20.378	-0.445	5.447	0.721
GWB2	2.954	2.332	26.346	-0.453	5.918	0.830
GWB3	2.733	2.321	24.388	-0.447	5.925	0.816
GWB4	2.507	2.200	21.271	-0.438	5.755	0.747
G WBK1	3.826	1.935	26.482	-0.462	5.647	0.906
G WBK2	4.578	2.181	30.970	-0.432	6.134	0.840
G WBK3	4.258	2.289	29.219	-0.489	6.459	0.984
G WBK4	3.746	1.976	23.906	-0.470	5.633	0.911
G WC1	3.139	2.932	25.623	0.009	19.500	0.993
G WC2	2.579	2.184	19.302	-0.450	19.171	0.649
G WC3	2.818	2.372	22.535	-0.453	7.830	0.661
G WC4	2.678	2.254	23.453	-0.447	7.424	0.647
GSoB1	2.154	4.517	12.856	-0.422	13.870	0.625
GSoB2	2.245	4.638	10.826	-0.402	15.660	0.659
GSoB3	2.498	5.073	12.515	-0.427	19.613	0.598
GSoB4	2.326	4.180	11.545	-0.394	16.279	0.702
GSoBK1	2.859	4.840	13.699	-0.429	19.461	0.666
GSoBK2	2.925	4.754	14.434	-0.463	18.602	0.886
GSoBK3	3.707	6.725	18.431	-0.416	22.652	0.711
GSoBK4	2.787	4.383	12.948	-0.449	18.456	0.716
GSoC1	2.820	6.145	13.446	-0.394	19.985	0.619
GSoC2	2.634	4.706	10.293	-0.453	18.658	0.689
GSoC3	3.071	7.015	14.222	-0.435	23.320	0.644
GSoC4	2.937	5.290	21.424	-0.430	19.624	0.676
GSpB1	4.150	16.360	12.623	-0.420	23.219	0.628
GSpB2	5.381	12.279	21.877	-0.465	24.405	0.676
GSpB3	4.288	14.958	37.787	-0.336	21.336	0.667
GSpB4	4.976	8.441	26.544	-0.373	25.703	0.718
GSpBK1	6.892	9.585	28.053	-0.423	19.406	0.712
GSpBK2	4.556	15.683	39.415	-0.465	17.852	0.604
GSpBK3	7.724	10.630	28.789	-0.474	28.616	0.620
GSpBK4	5.392	11.745	43.606	-0.309	17.505	0.606
GSpC1	3.838	14.107	31.102	-0.423	18.096	0.581
GSpC2	4.647	7.475	21.217	-0.386	23.613	0.540
GSpC3	3.968	13.489	30.829	-0.449	13.228	0.753
GSpC4	5.018	16.944	14.755	-0.431	20.347	0.641